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The Rev. William Gregor (1761–1817), discoverer of titanium.

By Sir Arthur Russell, Bart.

[Read November 5, 1953.]

IN view of the important uses to which the metal titanium has been applied in recent years, it seems fitting that some tribute should be paid to its Cornish discoverer, the Rev. William Gregor, and with this end in view I have collected the following facts concerning this now almost forgotten distinguished early chemist.

The Rev. William Gregor, M.A., chemist and mineralogist, was the younger son of Francis Gregor, member of an old Cornish family of Trewarthenic, Cornelly, Cornwall. Born on December 25, 1761, he was educated at Bristol Grammar School, and it was while there that he first developed a taste for chemistry. From Bristol he went to St. John's College, Cambridge, from 1780 to 1787, becoming a Platt fellow, his classical and mathematical attainments being of a high order. Ordained in 1787, he was appointed Rector of Diptford, Devonshire, and in 1790 married Charlotte Anne Gwatkin, daughter of a Bristol merchant, by whom he had one daughter. In 1793 he was presented with the living of Bratton Clovelly, Devonshire, but exchanged this in the same year for that of Creed, Cornwall, where he remained until his death in 1817. Gregor was made an honorary member of the Geological Society of London in the year of its inception, 1807, and was an original member of the Royal Geological Society of Cornwall on February 11, 1814. Among his intimate friends were his neighbour John Hawkins of Trewithen; Samuel Drew the Cornish metaphysician, the acquaintance of whom he made in 1803; and John Ayrton Paris, M.D., resident at Penzance from 1813 to 1817 and one of the founders of the Royal Geological Society of Cornwall.

It was at the remote and quiet vicarage of Creed (one mile south o Grampound) that this erudite, modest, and kindly man carried out, wit little or no convenience or apparatus, his original and for those day surprisingly accurate analyses of various Cornish minerals. The write has in his possession several letters written by Gregor in 1804 and 180 to John Hawkins, and from these an insight can be obtained of th painstaking enthusiasm he displayed in the analysing of minerals, bu never allowing his love for science to interfere with his parochial duties

Gregor's most important discovery, that of the metal titanium, wa occasioned by his analysis in 1790 of the mineral menaccanite (originall spelt menachanite or alternatively menacanite and menakanite), variety of ilmenite which occurred in the sand of a stream at Tregonwel Mill, Menaccan (also spelt Manaccan and Menachan), Cornwall. Thi he pronounced to be iron in a magnetic state, united to the calx o a new metallic substance which he proposed to call menacanite o menachine. His account of this mineral was first published in 1791 i German and French journals (see Bibliography). It was also read before the Royal Society of London, but the prior publication in a foreign journal prevented its insertion in the Philosophical Transactions. It was not until 1795 that M. H. Klaproth, on analysing rutile, called the new metal Titanium or Titankalk, and on subsequently analysing menaccanite and finding it contained the same metal, he graciously acknowledged Gregor's prior claim to the discovery. Gregor's choice o names for his new metal was unfortunate and naturally gave rise to ambiguity, there being no distinction between the mineral and the metal.

He subsequently determined the presence of titanium in corundum from Tibet, and in black tourmaline from the so-called tin floors at Botallack mine, St. Just, Cornwall. Of the former he wrote in a letter to John Hawkins, dated February 14, 1804: 'It was out of *respect* to the Royal Society and Sir Joseph Banks that I did not obtrude my Paper on a variety of Corundum, on them. Nothing but what is perfectly new and remarkable should, I think be inserted in "The Transactions" of that learned Body. There are many facts and observations, which are worthy of being preserved, but not worthy of a place in so good company Every reptile is not worthy of being preserved in proof-spirits.' Of the tourmaline he sent a crystallized specimen to James Sowerby who figured and described it in his 'British Mineralogy', 1809, vol. 3, plate 210, p. 19.

This same letter and one dated May 20, 1804, show that Gregor was

the first to examine chemically and describe the species wavellite, his experiments being performed on specimens of the mineral which he had collected at Stenna Gwyn mine, St. Stephen-in-Brannel, Cornwall, at the end of 1803. The results of his analysis on 30 grains were described by him in a paper in 1805. Later in the same year Humphry Davy and William Babington described the Devonshire wavellite (Phil. Trans., 1805, part 1, pp. 155–162), Davy proposing for it the name hydrargillite and Babington wavellite after Dr. W. Wavell of Barnstaple who had supplied the material. Both Gregor and Davy considered the mineral to be a hydrate of alumina. Gregor, however, had detected phosphoric acid and fluorine, although in the case of the former in so small quantity 'as not to admit of being subjected to experiment'. Davy, on the other hand, missed both the phosphoric acid and fluorine, hence his name hydrargillite. Gregor also describes his experiments on uran-glimmer (torbernite and autunite), from Stenna Gwyn mine, and deplores the fact that the mine had closed as he had insufficient material to complete his analysis; he adds 'I shall however rummage the piles and deads of the mine'.

The mineral scorodite had also received his attention, for James Sowerby in his 'British Mineralogy', 1817, vol. 5, plate 547, p. 275, figures and describes a massive specimen of this mineral 'broken from a rock on a down in the parish of Perranarworthal, Cornwall', which had been presented to him by Gregor in 1808 with the information that a preliminary chemical examination showed it to be an arsenate of iron. Scorodite, since Bournon first described it in 1801, had always been supposed to be a compound of iron, copper, and arsenic.

Gregor's attachment to Cornwall is shown in another letter written on February 5, 1807, to Hawkins congratulating him on having settled at Bignor Park, Sussex: 'You enjoy the great advantage of being at a commodious distance from London—We in this County are thrown too far off from that great source of information and entertainment. However, I am contented where I am—I have struck my root and could not bear to be transplanted even under a more genial sky without suffering inconvenience—How happy a circumstance it is, that we are so much the Children of Habit!'

He is described as having been a man of singular charm of character, and possessed of the highest intellectual qualities, though of a most modest disposition. He was an excellent and devoted parson, and in addition to his scientific attainments was a painter of landscapes, an etcher of considerable merit, and a musician. One of the first to

introduce vaccine inoculation in Cornwall, he succeeded in overcoming popular prejudice. Gregor died on July 11, 1817, from tuberculosis which had more or less incapacitated him during the last few years of his life, and was buried at Creed. Inquiries have failed to show that any portrait of him exists.

In 1818 John Ayrton Paris described, under the name gregorite, menaccanite sand which had been sent to him by Colonel Sandys from the latter's estate at Lanarth, St. Keverne, Cornwall.[1] G. J. Adam later applied the name gregorite to an impure bismuth carbonate agnesite, from St. Agnes, Cornwall, which had been analysed by Gregor (Tableau Minéralogique. Paris, 1869, p. 27). M. H. Klaproth, R. P. Greg and W. G. Lettsom, E. S. Dana, and others give Gregor's name as Macgregor in error. Gregor contributed many specimens to the John Hawkins collection and to that of Philip Rashleigh, amongst others stannite from Stenna Gwyn mine in 1800, and wavellite from the same locality in 1804, both of which are now in my collection.

The history of the exceedingly rare mineral fluellite is interesting, and may perhaps find a place here. Armand Lévy, while cataloguing the collection of Charles Hampden Turner, observed small crystals of an unknown mineral on a specimen of wavellite labelled 'Cornwall', but obviously from Stenna Gwyn mine, St. Stephen-in-Brannel, Cornwall. These crystals were examined by Dr. William Hyde Wollaston, who measured them, determined their refractive index, and found them to consist of alumina and fluoric acid, and he proposed the name fluellite for the mineral. These results were published by Lévy in 1824 (Ann. Phil., ser. 2, vol. 8, pp. 242–243) and thus to Lévy is usually ascribed the honour of first describing the species. James Sowerby, however, in his 'British Mineralogy', 1809, vol. 3, pp. 85–86, plate 243, gives an illustration, dated 1807, of a specimen of this mineral under the name of argilla hydrata, or hydrargillite, which had been obtained by Gregor from Stenna Gwyn mine. The fluellite crystals on this specimen are accompanied by wavellite, quartz, fluorite, and autunite. There are also given two quite accurate drawings of fluellite crystals. In determining the angles, which he gives roughly, of these minute crystals, Sowerby's son employed a microscope, and by holding a sheet of paper

[1] J. A. Paris, Trans. Roy. Geol. Soc. Cornwall, 1818, vol. 1, p. 226. [Min. Mag. 29–983.] It is interesting to note that according to a deed preserved in the Cornwall County Record Office, Truro, the grant of a sett, dated October 16, 1795, was given by Francis Gregor (elder brother of William) to Robert Were Fox and Andrew Fenton Ellis to work tin, copper, and menaccanite, in Penpol estate, St. Anthony in Meneage. This will have included the Tregonwell stream.

below, and on one side of the crystal, was able to draw on a large scale, angles, until one most closely approximating to that of the actual crystal was found. In the text Sowerby gives the results of Gregor's chemical examination of the mineral. This showed the presence of alumina, fluoric acid, and water, with traces of lime and silica. Both Gregor and Sowerby appear, however, to have confused the fluellite with the associated wavellite, although Gregor pointed out that the mineral in question seemed to differ from common hydrargillite (wavellite) in that it contained a larger proportion of fluoric acid, for he had in 1804–1805 examined chemically the wavellite from Stenna Gwyn mine. In 1847 Richard Talling, the mineral dealer of Lostwithiel, Cornwall, succeeded in rediscovering the mineral (letter dated March 24, 1847, in the Mineral Department, British Museum) of which previously only two or three specimens were known, at the original locality, Stenna Gwyn mine, at that time abandoned. In order to obtain the fluellite he evidently succeeded in entering the old adit, which then, as now, is flooded by a watercourse which passes its mouth. The specimens he collected in the summer of that year were all apparently broken from a single mass of vein-stuff, and though he made other attempts in succeeding years, he was unsuccessful in finding more (see R. P. Greg and W. G. Lettsom, 'Manual of the Mineralogy of Great Britain and Ireland', 1858, pp. 25–26). Many years ago the writer of these notes attempted to enter the adit, but found it impossible unless the water be diverted. However, in the summer of 1948, while we were showing a party of the International Geological Congress the Stenna Gwyn mine, my friend and colleague Mr. Arthur Kingsbury had the good fortune to find a specimen showing several well-defined crystals of fluellite in a block of vein-stuff built into the wall of a small ruined building on the mine.

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3. Analysis of a variety of corundum. Nicholson's Journ., 1803, vol. 4, pp. 209–214.

[Detailed account of the analysis of a specimen of lilac-coloured corundum from Tibet, given to Gregor by Philip Rashleigh.]

4. On the production of sulphate of magnesia from the ashes of pit-coal, with remarks on the efflorescence of the same salt, observed by Dr. Bostock. Ibid., 1803, vol. 5, pp. 225–227.
5. Experiments on a mineral substance formerly supposed to be zeolite; with some remarks on the species of uran-glimmer. Phil. Trans. 1805, vol. 95, pp. 331–348. Reprinted in Nicholson's Journ., 1806, ser. 2, vol. 13, p. 247.

   [Experiments on wavellite, torbernite, and autunite from Stenna Gwyn mine.]
6. On a native arseniate of lead. Phil. Trans., 1809, vol. 99, pp. 195–211; and Phil. Mag., 1810, vol. 35, pp. 87–94.

   [Description with analysis of mimetite from Wheal Unity, Gwennap, Cornwall. Gregor had in 1808 presented James Sowerby with a specimen of the Wheal Unity mimetite which had then only recently been found and of which an excellent plate is given in the latter's 'British Mineralogy', 1809, vol. 3, plate 295, pp. 187–190. Along with this is a full account of Gregor's analysis.]
7. Analysis of a soil containing free muriatic acid, and muriates of soda, lime, alumine, magnesia, and manganese. Nicholson's Journ., 1811, vol. 28, pp. 180–184.
8. Experiments upon green uran mica with a view to its chemical analysis. Ann. Phil., 1815, vol. 5, pp. 281–284.

   [Torbernite (meta-torbernite) from Old Gunnislake mine, Calstock, Cornwall. A partial analysis is given.]
9. On the tremolite of Cornwall. Trans. Geol. Soc. London, 1816, vol. 3, pp. 399–403. Also as a pamphlet with a title-page dated 1816.

   [An obscure mineral, not asbestos, from the picrite of Clicker Tor, Menheniot, Cornwall.]
10. Experiments on topaz, and carbonate of bismuth, with some observations relative to Smithson Tennant, Esq. Ann. Phil., 1816, vol. 8, pp. 276–279.

    [He ascertained the presence of potash in topaz from St. Michael's Mount, Cornwall, and in that from Scotland and Brazil. A mineral, possibly bismutite, from Wheal Coates, St. Agnes, Cornwall, he determined as being a mixed bismuth carbonate and oxide. James Sowerby in his 'British Mineralogy', 1811, vol. 4, p. 77, figures (the figure was drawn in 1809) and describes under the heading of 'Bismutum carbonatum' a specimen from St. Agnes, Cornwall, which had been sent to him by Gregor. This specimen found its way into the collection of Thomas Allan and later to the Allan-Greg collection, for in R. P. Greg and W. G. Lettsom's 'Manual of the Mineralogy of Great Britain and Ireland', 1858, p. 379, it is specifically mentioned as having passed under the name of carbonate of bismuth or agnesite, the latter so named by H. J. Brooke and W. H. Miller ('An elementary introduction to Mineralogy', by the late William Phillips, 1852, p. 591). On searching the Allan-Greg catalogue in the British Museum in 1935 it was found that this specimen had been given in exchange to Columbia

University, New York, but on Dr. W. Campbell Smith asking for the loan of it on behalf of the writer, the Columbia University authorities most graciously gave back the specimen to the British Museum. An examination of it showed that it is undoubtedly the actual specimen figured by Sowerby, but that it contains no bismuth, and is merely a mixture of a lithomarge-like mineral, quartz, and a little limonite. It is probable therefore that when Gregor presented the specimen to Sowerby he assumed it to be similar to the one which he had analysed.]

11. Observations on a remarkable change which metallic tin undergoes, under peculiar circumstances, and on its partial conversion into a muriate of tin. Trans. Roy. Geol. Soc. Cornwall, 1818, vol. 1, pp. 51–59.

[Describes the occurrence of tin chloride in masses of 'Jew's House Tin', anciently smelted tin found in boggy ground in Cornwall.]

12. On Kupfer-Nickel. Trans. Roy. Geol. Soc. Cornwall, 1818, vol. 1, pp. 224–225.

[Describes the occurrence and gives analyses of niccolite, and a mineral possibly gersdorffite, which had recently been found at Pengelly mine, St. Ewe, Cornwall.]

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Western Morning News newspaper, October 3, 1952.

Space lattices.

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[Read January 27, 1955.]

THE concept of a space lattice is fundamental in crystallography. A space lattice, or more simply a lattice, is an indefinitely extended regular array of points, in which the environment of each point is exactly the same. This implies that if the lattice is (1) translated parallel to itself, or (2) inverted about one of its points, or (3) rotated it will remain precisely the same as it was before such transformations. Such projective transformations as translation, inversion, or rotation are called symmetry operations. A lattice therefore may be said to be invariant in respect to certain specific symmetry operations. It is then said to possess certain symmetry elements. The fundamental symmetry operations are translations, inversions, and rotations. There is no symmetry element corresponding to translation, which is implicit in all lattices. Centres of symmetry correspond to inversion and axes of symmetry correspond to specific rotations. Points of mirror symmetry and lines of mirror symmetry may also be considered as fundamental elements of symmetry, but the plane of mirror symmetry is a composite element of symmetry, being the resultant of two-fold rotation followed by inversion.

There are in all twenty types of lattices, as defined by their symmetry element: one one-dimensional, five two-dimensional, and fourteen three-dimensional. All these lattices have an application in the study of material objects: one-dimensional lattice to the chain structural units of crystals, two-dimensional lattices to the sheet structural units of crystals, and three-dimensional lattices to the crystals themselves.

The number of lattices in a space of n-dimensions (S_n) is equal to the sum of squares of the first n members, i.e.

$$S_n = 1^2+2^2+\ldots+n^2 = \sum_{k=1}^{n} k^2.$$

This expression may be transformed into a polynomial of the third degree: $S_n = \frac{1}{3}n^3+\frac{1}{2}n^2+\frac{1}{6}n$, the solution of which for $n = 1, 2, 3$, is respectively 1, 5, 14.

This equation can only be verified for the spaces of one, two, and three dimensions, as space lattices in dimensions higher than three have not been as yet constructed.

Lattices are specified by their parameters. The one-dimensional lattice, or linear row of equally-spaced points, is specified by one parameter—by a vector length (a) of primitive translation; the two-dimensional lattice or net is specified by the two vector lengths (a, b) and the angle between them (γ); the three-dimensional lattice is specified by three vector lengths (a, b, c) and three angles between them (α, β, γ). The vector lengths are also referred to as 'axes' and the angles as 'direction angles'. All parameters may vary in respect of their relative equality: all unequal; two equal; all three equal. In addition, angle parameters may assume fixed values of 90° and 60° and also stand in certain relation to linear parameters.

It is very important to remember that the choice of axes of reference for each array of points is arbitrary and that each array of points may have a number of alternative systems of parameters. On the other hand, the symmetry elements of a lattice are absolutely fixed. Thus lattices may be specified by their parameters, but lattice types are defined by their elements of symmetry. Thus in a triclinic lattice the six parameters may exhibit innumerable variations, including that of two clino-angles and one right angle, but a diclinic lattice does not exist alongside the triclinic and monoclinic lattices.

Each lattice type, or more simply lattice, is characterized by an assemblage of symmetry elements. All lattices are formed by translations, and all are characterized by inversion, so that the diagnostic symmetry operations are the rotation and mirror reflections. The diagnostic elements of symmetry are therefore the points or axes of symmetry (A_2, A_3, A_4, A_6), and the points, lines, and planes of mirror symmetry (P). The degree of symmetry of a lattice is expressed by the symmetry number. As originally defined by W. H. Bragg,[1] 'symmetry number' is the number of assymetrical molecules in the unit cell of a molecular compound. In the case of lattices this number corresponds to the number of points generated by the operation of inversion, rotation, and reflection on one original point. For three-dimensional lattices the symmetry number is equal to the number of the general faces (hkl) or ($hk\bar{i}l$) of the holosymmetrical class of the corresponding system.

Lattices are also characterized, but not uniquely, by their degree of

[1] W. H. Bragg, The significance of crystal structure. Journ. Chem. Soc. London, 1922, vol. 121, pp. 2766–2787. [M.A. 2–328.]

reedom, which can be defined as the number of independent variable arameters which are needed to specify a lattice. The degree of freedom s equal to, or less than, the number of parameters. The degree of free- om is reduced when one or more parameters is given a fixed value such s equality to another parameter or, in the case of angle parameters, quality to 90° or 60°.

Figures relative to the two-dimensional and to the three-dimensional ttices are given in tables I and II. Symbols used for lattices are: L line) one-dimensional lattice: N (net) two-dimensional lattices, bearing ualifying subscripts (N_c, N_o, &c.): P primitive three-dimensional lat- ices, bearing qualifying subscripts; also C (c-face-centred); F (face- entred); and I (body-centred).

A one-dimensional lattice, or a line lattice, is a row of equally-spaced oints along a straight line of an indefinite length (geometrical lattices, n distinction to real crystals, have no boundary points). It has one legree of freedom—the linear parameter (a). Besides translation and nversion it is characterized by points of mirror symmetry (lattice points nd half-way points). In virtue of its one-dimensionality it cannot ossess either axes or planes of symmetry.

Two-dimensional lattices, plane-lattices or net lattices, can be postu- ated to be made of equally-spaced array of line lattices. In all, there are ive two-dimensional lattices, particulars of which are given in table I.

TABLE I. Two-dimensional lattices.

Symbol.	Mesh.	Parameters. Linear.	Angles.	Degree of freedom.	Points of rotation (A_n) and lines of mirror symmetry.	Sym- metry number.
N_c	Clino-	a b	γ	3	A_2	2
N_o	Ortho-	a b	90°	2	A_2, $2P$	4
N_r	Rhombo-	a a	γ	2	A_2, $2P$	4
N_t	Tetra-	a a	90°	1	A_4, A_2, $4P$	8
N_h	Hexa-	a a	60°	1	A_6, A_3, A_2, $6P$	12
		or a $b = a\sqrt{3}$	90°			

The nomenclature followed, namely clino-mesh, ortho-mesh, rhombo- nesh, tetra-mesh, and hexa-mesh, is that proposed by W. L. Bond.[1] Besides translation and inversion these lattices possess rotation points

[1] W. L. Bond, The fourteen space lattice. Univ. Toronto Studies, Geol. Ser., 1947, no. 51 (for 1946), pp. 9–20. [M.A. **10**–149.]

and lines of mirror symmetry. It is usual to divide two-dimensional lattices into four primitive (N_c, N_o, N_t, and N_h) and one compound (N_r) lattice. In accordance with this I have arranged the four primitive lattices along the cardinal points of a centred triangle and have placed the rhombo-lattice outside this triangle (fig. 1). As will be seen later,

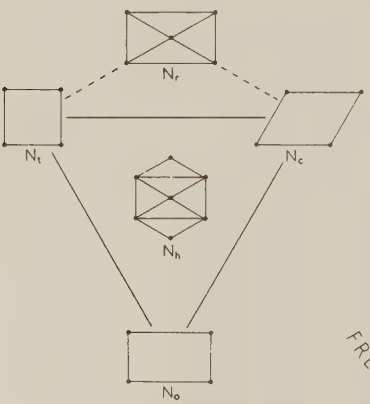

Fig. 1.

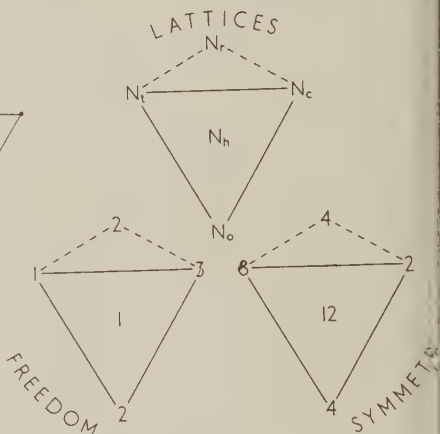

Fig. 2.

Two-dimensional lattices.

such a pattern has a direct relation to the pattern of the three-dimensional lattices. The double-triangle pattern of the two-dimensional lattices provides an arrangement in which there is a regular transition of the values of the degree of freedom and symmetry number of the lattices as shown graphically in fig. 2.

Other groupings are possible. For example, the rhombo-lattice may be called primitive and the ortho-lattice compound, as being derived by the combination of two N_r lattices. In the same way, the hexa-lattice may be considered to be formed from the combination of two N_o lattices. Such a principle of equivalence is a normal case among lattices and is constantly to be found among three-dimensional lattices. The choice of co-ordinate axes is also arbitrary. Thus the hexa-lattice can be referred to three axes of equal length at 120° to each other, or to two axes of equal length at 60° to each other, or to two axes a and $b - a\sqrt{3}$ at 90° to each other. Rhombo-lattice may also be referred to two axes of equal length, or two axes at right angles to each other (ortho-axes).

Three-dimensional lattices are usually divided into seven primitive and seven compound lattices, the total number being fourteen. The

principle of equivalence discussed above with regard to two-dimensional attices may be applied to some of these lattices, such, for example, to he hexagonal lattice or to the rhombohedral lattice. The same applies o the freedom of choice of axes of reference. Particulars for the seven primitive lattices are given in table II. Compound lattices have the

TABLE II. Primitive three-dimensional lattices.

Symbol.	Lattice.	Parameters. Linear.			Angles.			Degree of freedom.	Axes of rotation (A_n) and planes of mirror symmetry (P).	Symmetry number.
P_{tr}	Triclinic	a	b	c	α	β	γ	6	—	2
P_m	Monoclinic	a	b	c	90°	β	90°	4	A_2, P	4
P_o	Orthorhombic	a	b	c	90°	90°	90°	3	$3A_2$, $3P$	8
P_{te}	Tetragonal	a	a	c	90°	90°	90°	2	A_4, $4A_2$, $5P$	16
P_c	Cubic	a	a	a	90°	90°	90°	1	$3A_4$, $4A_3$, $6A_2$, $9P$	48
P_r	Rhombohedral	a	a	a	α	α	α	2	A_3, $3A_2$, $3P$	12
P_h	Hexagonal	a	$(a\sqrt{3})$	c	90°	90°	90°	2	A_6, $6A_2$, $7P$	24
		or								
		a	a	c	90°	90°	60°			

same symmetry and degree of freedom as their mother primitive lattices. The hexagonal lattice, for the sake of uniformity, is referred to a three-axial system. This, however, does not replace the four-axial system used in crystal morphology, but is introduced so that the hexagonal lattice can be compared and contrasted with the two neighbouring lattices - rhombohedral and orthorhombic.

The seven primitive three-dimensional lattices are arranged in a classificatory pattern which has the form of a centred hexagon (fig. 3). The seven compound lattices are arranged in places adjoining their mother lattices (fig. 4). The relation of this pattern to the patterns of the degrees of freedom and symmetry numbers of the seven primitive lattices is shown by means of a special diagram (fig. 5). It will be seen from this diagram that an attempt has been made to arrange lattices in such a way that, with some exceptions, the transition from one lattice into another is effected with a minimum change in the degree of freedom and symmetry number. According to their symmetry the seven lattices can be divided into three classes, which in the diagram form three distinct zones: high symmetry (P_c, P_h): medium symmetry (P_{te}, P_r); and low symmetry (P_o, P_m, P_{tr}).

In the hexagonal pattern the hexagonal circuit (P_{tr}, P_m, P_o, P_{te}, P_r) must be distinguished from the vertical diagonal traverse, in whi all the four lattices can be referred to the same system of orthorhomb

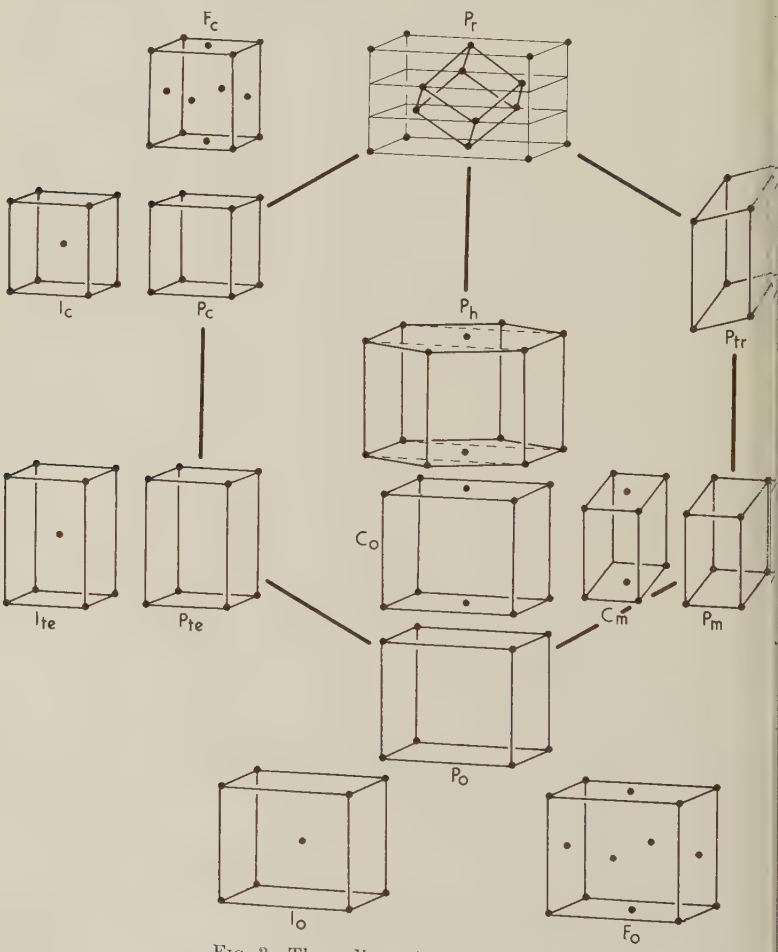

FIG. 3. Three-dimensional lattices.

axes, and can all be postulated to be modifications of the primitive orthorhombic lattice, in the following way:

$$C_o = 2P_o;\ P_h = C_o \text{ (at } b = a\sqrt{3});\ P_r = 3P_h,$$

with co-ordinate points (0, 0, 0), (0, 1/3, −1/3), (0, −1/3, 1/3); and $c \neq a\sqrt{3}/2$ (at $c = a\sqrt{3}/2$, P_r becomes P_c).

The triangular pattern of the two-dimensional lattices and the hexagonal pattern of the three-dimensional lattices provide two simple schemes of classification of these lattices on the basis of axes of refer-

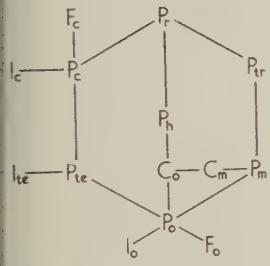

FIG. 4. Three-dimensional lattices.

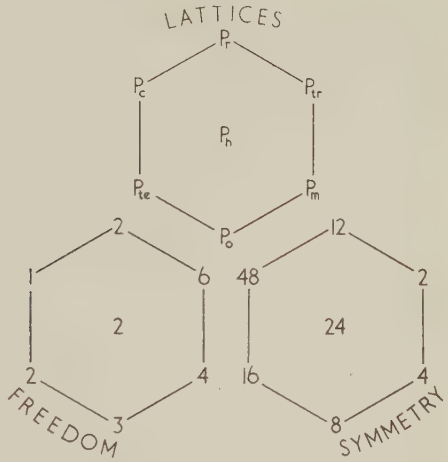

FIG. 5. Three-dimensional lattices.

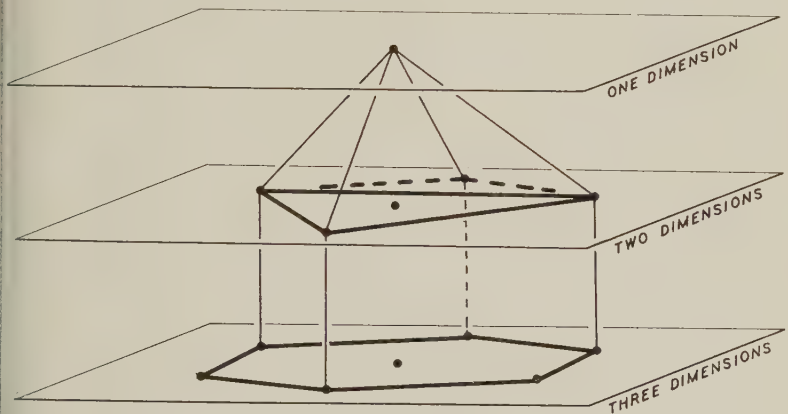

FIG. 6. Point relationship of 1-, 2-, and 3-dimensional lattices.

ence, degree of freedom, and symmetry number. But the net lattices are generated by the line lattices, and the three-dimensional lattices are generated by the net lattices. This means that all the twenty lattices can be brought together into one scheme of classification. This can be

done by means of three horizontal parallel planes (fig. 6). The upper plane contains one point only, corresponding to one line lattice. The middle plane contains five points corresponding to the net lattices arranged in a double triangle pattern. The lower plane contains the fourteen three-dimensional lattices arranged about the hexagonal pattern. Remembering that P_{tr} is generated by three N_c; P_o by three N_o; P_c by three N_t; P_r by three N_r; and P_h by one N_h and two N_t; we can place the generating net lattices above the generated three-dimensional lattices, N_c above P_{tr}; N_o above P_o; N_t above P_c; N_r above P_r; and N_h above P_h. This diagram is a graphical representation of the twenty lattices in their genetic relationships and in a general way it summarizes our knowledge of all lattices.

The whole scheme can be easily remembered: point, triangle, hexagon, corresponding respectively to one-, two-, three-dimensions. It is a harmonious and interconnected system of lattices.

In conclusion, I would like to thank Dr. K. M. Jack and Mr. F. F. Bonsall for their friendly advice, and Mr. J. Lee for his help with the illustrations.

Manganese amphiboles from Chikla, Bhandara district, India.

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[Read March 25, 1954.]

Introduction.

THE four amphiboles described in this paper were collected during the summer of 1950 from the Sitasaongi mine. This mine, which produces high-grade manganese ore, is situated in the Chikla area, Bhandara district, India. The ore band is 8 to 18 feet thick and is strongly

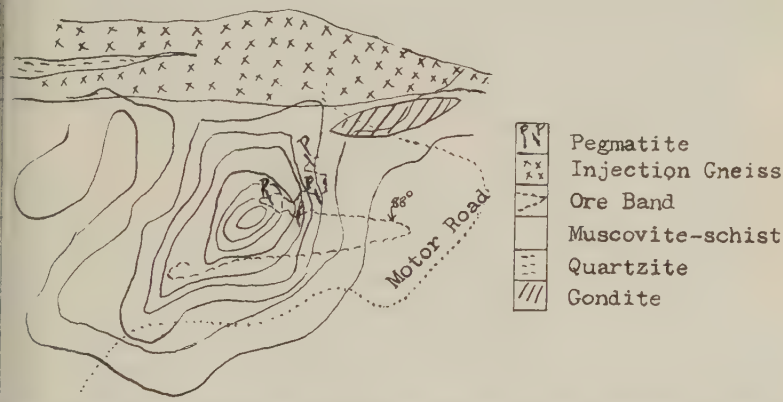

Fig. 1. Geological map of Sitasaongi hill, Chikla, India. (Scale, $3\frac{1}{3}$ inches = 1 mile.)

folded and faulted at many places (fig. 1). The most common rock types in the area are: calc-granulites, calc-gneisses, mica-schists, quartzites, gondite (quartz-spessartine-rock), injection gneisses, and pegmatites. The pegmatites are the youngest and cut through the manganese-ore band as well as the country-rocks. All are of Archaean age.

Previous work.

Of the four amphiboles described here, winchite and juddite were first described by Fermor (1909). Juddite was named on its optical properties, mainly pleochroism, while winchite was described in greater detail

and a chemical analysis of the mineral was given. Krishnan (1937) als reported the occurrence of winchite from Gangpur State, India, bu no optical properties of the mineral were given. Tirodite, named afte Tirodi mine, Balaghat district, India, was first described by Dunn a Roy (1938) and a chemical analysis of the mineral together with t

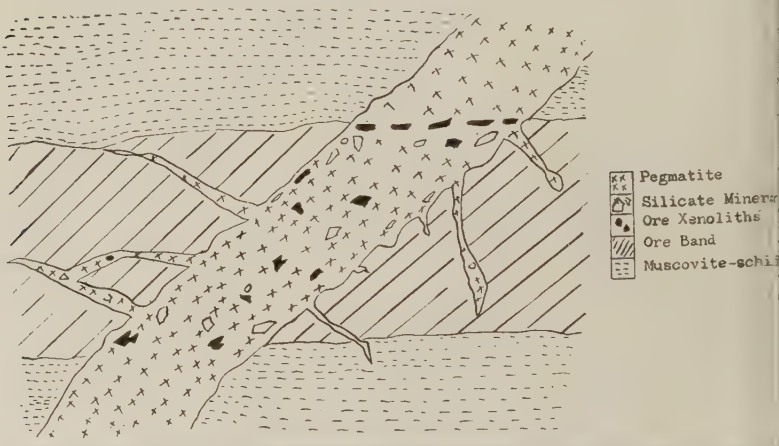

FIG. 2. Plan at the 60-foot level of the Sitasaongi mine, Chikla, India, showing the pegmatite cutting through the ore band.

physical and optical properties was presented. A preliminary descrip tion of these minerals from Chikla was given by Bilgrami (1953). Kil pady and Dave (1954) have also described manganese amphiboles from Balaghat district, India, and have given their optical properties and manganese contents. *Chiklite*, named after Chikla area, in which it is found, is here described for the first time, and its optical and chemica properties do not resemble closely any known amphibole.

OCCURRENCE.

Winchite, tirodite, juddite, and chiklite occur at Chikla in the pegma tite where it cuts the manganese-ore band and muscovite-schist at th 60-foot level of the Sitasaongi mine (fig. 2). Here the amphiboles ar accompanied by other manganese-bearing minerals, blanfordite, alur gite, manganophyllite, piedmontite, and rhodonite. Other mineral present are quartz, oligoclase, microcline, and a little baryte. Some o the minerals attain large dimensions and measure up to 3 inches in length.

Winchite occurs in a band of medium-grained felspathic gneiss associated with mica-schist and when freshly broken shows numerous blue-coloured needles. It is associated with quartz, oligoclase, alurgite, rutile, and a little manganese ore, probably braunite. In thin sections it occurs as anhedral crystals showing perfect amphibole cleavages and pink to blue pleochroism. Inclusions of quartz, manganese ore, and rutile are common (fig. 3).

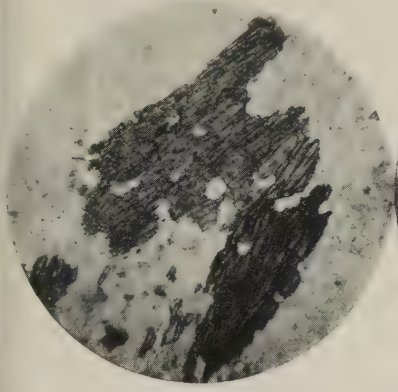

Fig. 3.

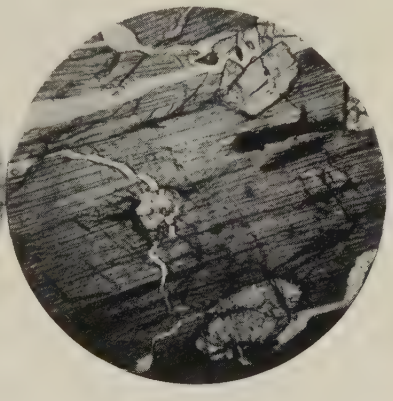

Fig. 4.

Fig. 3. Winchite with inclusions of quartz (white), rutile, and manganese ore (dark). ×20.

Fig. 4. Tirodite with inclusions of apatite and alteration veins (black). ×20.

Tirodite. Of the four amphiboles, tirodite is the simplest to recognize in the hand-specimen, due to its honey-yellow colour and stout prismatic habit; when crushed it breaks into fine asbestos-like silky fibres. In thin sections the mineral is straw-yellow in colour and shows perfect prismatic cleavages. Inclusions of euhedral apatite arranged roughly parallel to the cleavages are common (fig. 4). The mineral shows ultra-polarization colours due to high dispersion, and it is occasionally weakly zoned. Alteration of the mineral along the cleavages to a dense brown mass, probably psilomelane, is common.

A specimen of tirodite from manganese deposits of India was kindly presented by Mr. E. H. Shackleton of Whitehaven, Cumberland. The mineral is dark brown in colour, is less fibrous than the Chikla specimen, and under the microscope shows pale pink colour and a lower dispersion. The mineral is altered to a dense brown mass, probably psilomelane, and the brown colour of the hand-specimen is probably due to this mineral.

The MnO content of this specimen is 3·67 %, and γ (for Na-light) 1·649, and 2V $\neq$ 41°. Another specimen of the mineral was found by the author on a dump of Indian manganese ore belonging to The General Iron and Steel Co. Ltd., Workington. In this specimen the tirodite occurs as plates flattened parallel to the prismatic cleavages and without systematic orientation, forming an encrustation on braunite. Under the

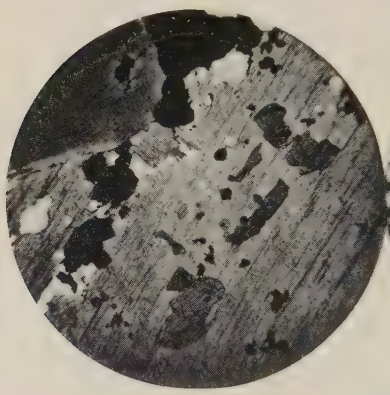

Fig. 5.

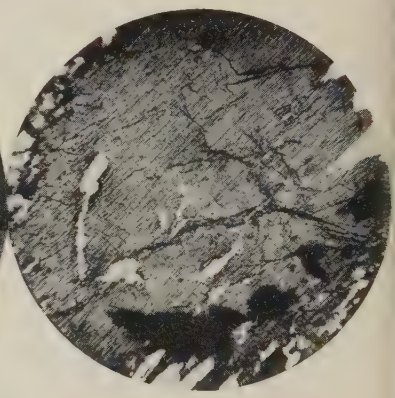

Fig. 6.

Fig. 5. Juddite with inclusions of manganese ore (black), baryte (white), and chiklite. ×20.

Fig. 6. Chiklite showing prismatic cleavage and alteration veins. ×20.

microscope the mineral is feebly pink to colourless and shows a lower dispersion than the Chikla specimen. The MnO content is 3·41, and γ 1·649 and 2V 42°.

Juddite shows anhedral form, rather poor prismatic cleavages and strong pleochroism. In thin sections and grains the mineral is pleochroic from carmine to red. Inclusions of manganese ore, baryte, and chiklite are common (fig. 5), and lie either parallel to the prismatic cleavages or are slightly inclined to them. Under crossed nicols the mineral shows strain effects round the inclusions, and in general large plates of the mineral show undulose extinction. Ultra-polarization colours due to very high dispersion are very characteristic.

Chiklite, by virtue of its deep violet colour and well-developed (100) and (110) forms, is quite distinct in the hand-specimen. It has pearly lustre on the cleavage faces, and the streak is very pale violet in colour. In thin sections the mineral resembles juddite, particularly in its pleochroic scheme, but the prismatic cleavages are better developed (fig. 6).

Faint zoning is occasionally present and patchy polarization is characteristic. Thin veins of a brown alteration product, probably limonite, are present.

Separation of the minerals.

Separation of the minerals for chemical analysis did not present any special problems. Winchite, which is associated with manganese ore, quartz, felspar, rutile, and a little mica, was separated by crushing the rock to 60-mesh British standard sieves and passing the powder through bromoform. From the heavy fraction winchite was separated from other heavy minerals by methylene iodide. The sample was further purified by crushing to 100-mesh followed by centrifuging in methylene iodide. The pegmatite amphiboles were separated by crushing the sample to $\frac{1}{8}$-inch size and hand-picking under a binocular microscope. The majority of the composite grains and those containing inclusions were removed by further crushing to $\frac{1}{16}$ inch and hand-picking. The final purification was effected by crushing to 100-mesh and centrifuging in methylene iodide and Clerici's solutions.

Chemical composition.

The structural formula generally accepted for the amphibole group is $X_{2\ 3}Y_5Z_8O_{22}(OH,F,Cl)_2$ where the X group mainly consists of Na, Ca, K, Mn (in part), the Y group of Al, Ti, Cr, Fe″, Mg, Li, Fe‴, Zn, Mn (in part), and the Z group of Si, Al, and possibly of Ti. The ionic replacements in this group of minerals are still imperfectly understood and it is possible that Ca ions as well as Mn may occupy both X and Y positions in the structure. The replacements may be regarded as giving rise to two structural types: (*a*) such that the number of cations remains 7; and (*b*) where the vacant spaces are partially or completely occupied by Na or K, and the number of cations varies from 7 to 8. It was originally suggested by Warren (1930) that the occupation of vacant spaces in tremolite by Na and K was related to the replacement of Si by Al in the band framework.

The chemical composition of the amphiboles under review, and their structural formulae calculated on the basis of 24(O,OH,F), are given in tables I and II. They emphasize the extreme flexibility of the amphibole constitution, and the significance of substitution of cations in the X, Y, and Z groups. The low Al content of these amphiboles, all of which is in four-fold co-ordination, is noteworthy. Al occurs in increasing amounts in six-fold co-ordination with the increasing temperature, and in the

present case points to the relatively low-temperature paragenesis of these amphiboles. Harry (1950) has pointed out that the amount of tetrahedrally co-ordinated Al in the metamorphic calciferous amphiboles appears to be related to the temperature of crystallization. The relationships in these amphiboles of Ca and Mn is of interest. In general chemical characteristics winchite resembles imerinite (table I, 3) and tirodite resembles richterite (table I, 7), but juddite and chiklite show no close comparisons with other known amphiboles. In winchite and tirodite all the Ca and Mn occupy X or some of the vacant positions, while in juddite and chiklite the Mn is presumably restricted to the Y positions and the Ca in part or whole is located in the Y positions.

TABLE I. Chemical analyses of winchite and tirodite with comparisons.

	1.	2.	3.	4.	5.	6.
SiO_2	55·14	55·64	53·73	53·26	53·26	53·25
Al_2O_3 ...	1·14	1·08	2·72	2·26	1·25	2·31
TiO_2	0·50	—	0·41	0·78	—	0·79
Fe_2O_3 ...	4·59	—	4·72	2·60	2·63	1·81
FeO	1·25	6·35	4·70	1·12	1·06	1·62
MgO	22·16	22·09	20·60	29·16	31·26	28·42
MnO	1·38	0·77	—	6·24	8·25	4·66
CaO	7·37	7·64	2·73	1·10	1·11	3·42
Na_2O	2·88	2·89	7·42	1·39	1·56	1·25
K_2O	1·24	0·98	1·82	0·09	0·07	0·06
H_2O+ ...	1·98	2·95	0·85	1·87	0·05	2·04
H_2O- ...	—	0·14	—	—	—	—
F	—	—	0·92	—	—	—
	99·63	100·53	100·62	99·87	100·50	99·63
Sp. gr. ...	2·970	2·959–3·024	—	3·252	3·312	3·248
α	1·636	—	—	1·629	1·629	1·629
β	1·646	—	—	—	1·639	—
γ	1·658	—	—	1·650	1·650	1·650
$\gamma-\alpha$	0·020	0·020–0·030	—	0·021	0·021	0·021
$\gamma:c$	18°	$\alpha:c$ 20–26°	—	17°	21°	18°
2V	82°	—	—	37°	88°	41°

1. Winchite, Chikla, India. Analyst, R. K. Phillips. Analysis on air-dried powder at 105° C.
2. Winchite, Kajlidongri, Central India. Analyst, T. R. Blyth (Fermor, 1909, p. 156).
3. Imerinite, Imeria, Madagascar. Analyst, F. Pisani (A. Lacroix, Min. France, 1910, vol. 4, p. 787).
4. Tirodite, Chikla, India. Analyst, R. K. Phillips. Analysis on air-dried powder at 105° C.
5. Tirodite, Tirodi mine, Central Provinces, India. Analyst, P. C. Roy (Dunn and Roy, 1938). [M.A. 7-317.]
6. Tirodite, Tirodi mine, Central Provinces, India. Analyst, S. A. Bilgrami. Analysis on air-dried powder at 105° C.

TABLE I (*contd.*). Chemical analyses of juddite and chiklite with comparisons.

	7.	8.	9.	10.	11.
SiO_2	57·74	51·21	57·10	52·66	48·51
Al_2O_3	0·37	2·82	6·19	1·75	1·08
TiO_2	trace	1·62	0·35	0·60	1·10
Fe_2O_3 ...	0·29	9·15	8·01	18·44	17·53
FeO	trace	0·97	2·69	0·86	14·31
MgO	23·67	11·31	9·13	6·29	1·31
MnO	2·40	7·69	0·34	2·55	0·66
CaO	9·01	3·91	0·31	7·80	5·43
Na_2O	3·14	8·97	9·77	7·29	7·87
K_2O	0·64	0·22	2·38	nil	1·48
H_2O+ ... }	2·39	1·89	0·50	1·88	1·48
H_2O- ... }		—	0·08	—	0·17
F	0·37	—	2·69	—	—
	100·02	99·76	101·28*	100·12	100·93
Less O for F	0·16	—	1·13	—	—
	99·86	99·76	100·15	100·12	100·93
Sp. gr. ...	2·99	3·27	—	3·44	—
α	1·605	1·667	—	1·685	—
β	—	1·683	—	1·700	—
γ	1·627	1·692	—	1·712	—
$\gamma-\alpha$	0·022	0·025	—	0·027	—
$\gamma:c$	17°	3°	—	8°	$\alpha:c$ 5–6°
2V	—	82°	—	82°	—

7. Richterite, Långban, Sweden. Analyst, A. Bygdén (Sundius, 1945). [M.A. **9**–271.]
8. Juddite, Chikla, India. Analyst, R. K. Phillips. Analysis on air-dried powder at 105° C.
9. Eckermannite, Norra Kärr, Sweden. Analyst, A. Bygdén (Sundius, 1946 *a*). Total* includes LiO_2 1·15, ZnO 0·59. [M.A. **10**–8.]
10. Chiklite, Chikla, India. Analyst, R. K. Phillips. Analysis on air-dried powder at 105° C.
11. Arfvedsonite, Morotu, Sakhalin. (K. Yagi, 1953.)

Winchite differs from ideal tremolite formula in containing 0·99 atom of Na and K and therefore is nearest to the end-member $NaCa_2Mg_5AlSi_7O_{22}(OH)_2$ of Sundius (1946*b*). The deficiency of Si-Al in the *Z* group shown both by these minerals from the type area and from Chikla is noteworthy.

The original analysis of tirodite shows some marked difference compared with both the analyses of the same mineral from the type locality, and also from the composition of the mineral from Chikla, the main difference being the absence of TiO_2 and the very low water content of the type material. The negligible amount of structural water reported in the earlier analysis suggests that it is inaccurate. The cell dimensions of the Chikla mineral were kindly determined by Dr. J. Zussman and

are a 9·80, b 17·97, c 5·30 Å., β 103° 9′. Measurements made on the specimen from the type area gave the same dimensions, within the limits of experimental error, as the Chikla specimen. The composition of tirodite shows a resemblance to that of winchite, the deficiency in the Z group of tirodite from the type area and the low Al and high Mg content being the common features. The main difference in the composition of the two minerals lies in their contrasted Ca and Mn contents, Ca being low and Mn high in tirodite, a reverse relationship being characteristic of winchite.

In juddite 2·5 atoms of Na are present in the formula unit. Thus, if juddite is considered as a derivative of tremolite, one Na atom occupies a vacant position and the remainder replaces Ca in the X position. This, together with the replacement of 0·5 atom of Si by Al, necessitates the presence of a relatively high proportion of trivalent ions in the Y position, a requirement met by the high ferric iron content of the mineral. Juddite may be compared with eckermannite (table I, 9) except in its

TABLE II. Calculation of analyses (table I) on basis of 24(O,OH,F).

	1. Winchite, Chikla.			2. Winchite, Kajlidongri.		
SiO_2	55·14	7·70	7·88	55·64	7·19	7·73
Al_2O_3... ...	1·14	0·18		1·08	0·54	
TiO_2	0·50	0·05		—	—	
Fe_2O_3... ...	4·59	0·48	5·26	—	—	
FeO	1·25	0·14		6·35	0·73	5·31
MgO	22·16	4·59		22·09	4·58	
MnO	1·38	0·15		0·77	0·09	
CaO	7·37	1·16	2·30	7·64	1·13	2·16
Na_2O... ...	2·88	0·78		2·89	0·78	
K_2O	1·24	0·21		0·98	0·16	
H_2O	1·98	1·84	1·84	3·09	1·37	1·37
	99·63			100·53		

	4. Tirodite, Chikla.			5. Tirodite, Tirodi.		
SiO_2	53·26	7·38	8·04	53·26	7·56	7·77
Al_2O_3 ...	2·26	0·66		1·25	0·21	
TiO_2	0·78	0·08		—	—	
Fe_2O_3 ...	2·60	0·27		2·63	0·27	
FeO	1·12	0·12		1·06	0·12	
MgO	29·16	6·02	7·76	31·26	6·05	
MnO	6·24	0·73		8·25	0·98	7·99
CaO	1·10	0·16		1·11	0·15	
Na_2O... ...	1·39	0·37		1·56	0·41	
K_2O	0·09	0·01		0·07	0·01	
H_2O	1·87	1·72	1·72	0·05	0·00	0·00
	99·87			100·50		

TABLE II (*contd.*)

	6. Tirodite, Tirodi.			8. Juddite, Chikla.			
SiO_2	53·25	7·29	7·82	51·21	7·52		8·00
Al_2O_3... ...	2·31	0·52		2·82	0·48		
TiO_2	0·79	0·16		1·62	0·17		
Fe_2O_3... ...	1·81	0·18		9·15	1·01		
FeO	1·62	0·18		0·97	0·11		5·00
MgO	28·42	5·88		11·31	2·49		
MnO	4·66	0·54	7·77	7·69	0·95		
CaO	3·42	0·51		3·91	0·61	0·28	
Na_2O... ...	1·25	0·32		8·97	2·54	0·33	2·91
K_2O	0·06	0·00		0·22	0·04		
H_2O	2·04	1·86	1·86	1·89	1·85		1·85
	99·63			99·76			

	10. Chiklite, Chikla.				
SiO_2	52·66	7·70			8·00
Al_2O_3... ...	1·75	0·30			
TiO_2	0·60	0·07			
Fe_2O_3... ...	18·44	2·05			
FeO	0·86	0·10			5·00
MgO	6·29	1·37			
MnO	2·55	0·31			
CaO	7·80	1·21	1·17		
K_2O	nil	nil	0·04		2·11
Na_2O... ...	7·29	2·07			
H_2O	1·88	1·82			1·82
	100·12				

high percentage of manganese atoms. When the composition of juddite is plotted on the cummingtonite-grunerite series composition-refractive index curves (Winchell, 1951), lower values for refractive indices than the determined values are obtained and this is probably related to the high content of manganese. Juddite may more appropriately be called ferririchterite.

Chiklite shows many of the chemical characteristics of juddite but is an amphibole of $X + Y = 7$ type. Considerations of the number of ions in the unit cell suggest that the X positions are occupied by Na atoms and that the whole of the Ca is located in the Y position. In this respect chiklite appears to be unique among known amphiboles. An arfvedsonite described by Yagi (1953, table I, 11) is similarly lacking in Y position atoms unless most of the Ca is assumed to occupy similar positions. This mineral differs from chiklite in being an amphibole of $X + Y = 8$ type. In both these amphiboles the high content of ferric iron and Na are noteworthy. Like juddite, lower refractive indices values are obtained from Winchell's curves compared with the determined values,

but here the discrepancy may be due to very high Fe‴ content of the mineral.

Distribution of trace elements.

The results of the spectrographic examination of the amphiboles under review are given in table III. It is interesting to note that win-

Table III. Spectrographic analyses of the amphiboles and muscovite-schist, showing the distribution of trace elements. (Parts per million ±50 %.)

	Winchite.	Juddite.	Chiklite.	Tirodite (Chikla).	Tirodite (type).	Mica-schist.
Cr	500	20	20	50	0	70
Co	20	50	10	70	100	20
Ni	150	100	30	300	250	100
V	10	10	0	0	20	150
Cu	50	30	30	150	100	50
Ba	400	50	1000	300	200	600
Sr	600	1500	300	800	20	80
Zr	20	0	20	10	10	50
Li	3	3	1	1	0	2
Mo	1	0	½	½	1	0
Ga	1	0	0	2	1	3
Bi	2	0	0	2	0	0
Pb	0	1	2	0	0	1

chite, the amphibole from the gneiss, shows little difference from the pegmatite amphiboles, the most marked difference is the high concentration of Cr which is low in the other amphiboles. It will be seen that Ni follows Mg closely and those amphiboles high in Mg are also high in Ni. Another interesting feature is that Cr does not follow Fe, nor do Ba and Sr follow K and Ca. The two specimens of tirodite, one from the type area and the other from Chikla, show resemblances in most cases. The notable difference is that Cr, Ba, and Sr are high in the Chikla specimen and low in the specimen from the type area.

Relation between the chemical composition, colour, and optical properties.

The problem of absorption colours in minerals is still imperfectly understood; a review of the literature on the subject brings out the following points:

(1) Magnesia has the effect of diluting or masking the colour produced by Ti, but in the case of tourmalines it has no effect on the colours produced by Fe and Mn.

(2) The colour produced by Ti dominates over that produced by Fe.

(3) The colour in biotites is related to their Fe content.
(4) The absolute proportion of any oxide responsible for a particular colour is less important than the proportion of the oxide to others present.
(5) Ions in a higher state of oxidation exert greater influence than those in a lower state of oxidation.

In the absence of specific data concerning the influence of a given element on the colour of the amphiboles, it is likely that points 4 and 5 are of greater importance. Thus, it is interesting to note that winchite, which has a lower magnesia content, is pleochroic in pinks and blues, while tirodite with higher magnesia is almost colourless. In the case of juddite and chiklite the very high ferric oxide content may be responsible for their colours.

No definite relationship between the chemical composition and optical properties is apparent except that the magnesia : iron ratio ($FeO+Fe_2O_3$ calculated as FeO) shows normal influence on the refractive indices. Winchite and tirodite with high magnesia : iron ratio show low refractive indices, while juddite and chiklite with low ratios show high refractive indices. It would appear from analyses 4 and 6 (table I) that the increase in MnO in tirodite tends to decrease the optic axial angle.

Paragenesis.

Fermor, when describing the manganiferous amphiboles from India, stated that 'all the known occurrences of amphiboles in Indian manganiferous rocks are the varieties that I look upon as metamorphic in origin, belonging always to the gondite series' (1909, p. 145). In another place, when discussing the origin of rhodonite, he again advocates a metamorphic origin, stating 'that the metamorphic mode of formation is the characteristic one is shown by the frequency with which this mineral occurs in the rocks of gondite series' (p. 141). The abundance of this mineral in the manganiferous rocks, he suggests, is due to 'the frequency with which the original sediments from which the gondite series were formed contained a high percentage of manganese' (p. 142). This explanation seems to hold in the case of winchite where it appears that the mineral was probably formed by the recrystallization of sediments which contained an appreciable amount of manganese. This explanation, however, does not hold in the case of pegmatite amphiboles. Here it is clear from the field evidence that assimilation of manganese ore and mica-schist by the pegmatite has taken place. Thus the formation of

rhodonite may be illustrated by the equation:

$$2Mn_2O_3+4SiO_2 = 4MnSiO_3+O_2,$$

the oxygen liberated oxidizing the ferrous to ferric iron, thus explaining the high ferric iron content of chiklite and other pegmatite amphiboles.

In view of its paragenesis and the lack of an abnormal content of magnesium in the composition of the mica-schist (table IV) it is difficult to account for the very high content of magnesium in the tirodite.

TABLE IV. Analysis of mica-schist from 60-foot level, Sitasaongi mine, Chikla. (Analyst, S. A. Bilgrami.)

SiO_2 ...	... 60·99	CaO ...	... trace
TiO_2 ...	... 1·21	Na_2O ...	... 0·75
Al_2O_3 ...	... 23·42	K_2O ...	... 3·97
Fe_2O_3 ...	... 1·49	P_2O_5 ...	... 0·05
FeO ...	... 0·56	H_2O+ ...	... 3·49
MnO ...	... 0·82	H_2O- ...	... 0·21
MgO ...	... 3·35		100·31

It is, however, noteworthy that the tirodite is confined to the margin of the pegmatite, while other amphiboles are found in the core. Thus it is possible that on assimilation of the schist and ore band the magnesia was taken up early in the formation of tirodite and led to a relative concentration of iron and sodium which are characteristically high in both juddite and chiklite.

Acknowledgements.—This work was carried out at the Geological Laboratories, University of Manchester, and I am indebted to Professor W. A. Deer for constant encouragement and helpful criticism of the paper. Thanks are due to the Central Provinces Manganese Ore Co. Ltd., Nagpur, India, for providing all possible facilities during the field work, to Mr. R. K. Phillips for the chemical analyses, and to Mr. P. A. Mohr for the spectrographic analyses.

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Grovesite, the manganese-rich analogue of berthierine.

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[Read March 24, 1955.]

A DARK brown (blackish-brown) mineral forms a thin crust on manganese ore on the specimen [B.M. 1944,35] from no. 5 ore-body of the Benallt mine, Rhiw, Carnarvonshire, North Wales. This is the specimen on which the first measurable crystals of banalsite were discovered in 1944 (Min. Mag., 1945, vol. 27, pp. 63 64). The mineral occurs as closely-packed, small rosettes, at most 0·5 mm. across, and is partly coated with a thin layer of baryte. An X-ray photograph by Dr. Bannister suggested that the mineral might belong to the chlorite group. Its optical properties were determined and nothing further was done with it at the time. When detailed work was started on the brown chlorite from veinlets in other specimens of the Benallt ore and more X-ray photographs were taken it was at once noticed that there were significant differences between the chlorite we have described and named pennantite (Min. Mag., 1946, vol. 27, pp. 217 220) and the chlorite-like mineral of the dark-brown rosettes first examined from no. 5 ore-body.

The mineral from no. 5 ore-body [B.M. 1944,35] was then carefully re-examined. It appears to be uniaxial, negative. Its pleochroism and absorption are similar to those of pennantite; $\beta = \gamma$, parallel to the cleavage, very dark brown, α perpendicular to the cleavage, red-brown: $\beta = \gamma > \alpha$. Refractive indices for Na-light are α' 1·658±0·001, $\beta = \gamma$ 1·667±0·001; slightly higher than for pennantite α' 1·646±0·001, $\beta = \gamma$ 1·661±0·001. This implies a higher birefringence for pennantite, but it is to be noted that the determinations of α are dependent on observations on flakes resting edge-on and vertical and consequently are less reliable than determinations for γ and β made on flakes lying flat. One can only claim that the lowest refractive indices so far measured on the two minerals are as given above.

As the X-ray photographs revealed interesting differences, it was decided to obtain sufficient of the pure mineral for micro-analysis. Thin pieces of the 'chlorite' crust were cut from the specimen, freed from ore by careful chipping and hand-picking, and then purified, as was done

for pennantite, by density and magnetic separations. About 150 mg. of very pure material was obtained and 70 mg. was used for a micro analysis, additional separate portions being used for determination of H_2O (60 mg.) and of the state of oxidation of the manganese and iron (20 mg.). The analysis was made by the same methods as were used for pennantite (loc. cit., p. 219).

The complete micro-analysis is given in table I, together with th

TABLE I. Chemical analysis and empirical unit-cell contents of grovesite.

			%					
SiO_2	...	...	22·0	Si	...	...	5·37±0·13	2·63 } 8·00
Al_2O_3	...	...	18·8	Al	...	...	5·41 _ 0·16	2·78
Fe_2O_3	...	...	4·1	Fe	...	...	0·75±0·02	
MnO	...	...	43·4	Mn	...	...	8·97±0·14	} 12·82
MgO	...	...	0·8	Mg	...	...	0·29±0·04	
BaO	...	...	0·3	Ba	...	...	0·03±0·01	
H_2O	...	...	9·0	Total cations		...	20·82±0·50	
			98·4	OH	...	...	14·54±0·51	
				O	...	...	22·02±0·29	
				(O+OH)		...	36·56±0·45	

The 'probable errors' are calculated, assuming maximum probable errors o 0·5 % in the MnO, SiO_2, and Al_2O_3, of 0·1 % in the Fe_2O_3, MgO, and BaO, and o 0·3 % in the H_2O; 0·02 Å. in a and b, 0·04 Å. in c, and 0·02 in the density, by the method described by one of the authors (Min. Mag., 1954, vol. 30, p. 481).

empirical unit-cell contents calculated using the measured density of the analysed sample and the cell dimensions obtained from the X-ray photographs. The chemical composition is practically the same as that of pennantite.

The density of D_4^{16} · 3·150±0·02 is also closely comparable to the value obtained on the analysed sample of pennantite, which was 3·06±0·02 (but there is reason to suspect that this figure may be a little low). The unit-cell dimensions are

$$a\ 5{\cdot}51\pm0{\cdot}02, \qquad b\ 9{\cdot}54\pm0{\cdot}02, \qquad c\ 14{\cdot}36\pm0{\cdot}04\ \text{Å}.$$

From these we deduce the chemical formula

$$4[(Mn,Mg,Al)_3(Si,Al)_2(O,OH)_9].$$

In 1946, when the above observations were made, the X-ray powder and rotation photographs of the new mineral were compared with those of a variety of chlorites and a number of other manganese silicates and aluminosilicates; but no resemblances sufficiently extensive to suggest

structural similarity were found. Recently the possibility occurred to one of the authors (M.H.H.) that the new mineral might bear a relation to the chlorite, pennantite, similar to that between berthierine[1] and chamosite. Comparison confirmed this idea. While X-ray powder photographs of pennantite closely resemble those of the other chlorites, and especially the iron-rich members such as thuringite and chamosite, those of the new mineral closely resemble powder photographs of cronstedtite and berthierine. There is one notable difference: the new mineral shows a fairly strong line corresponding to a spacing of 14 Å., which has not been recorded for cronstedtite or berthierine.

It is clear that the new mineral is not a chlorite, but a member of the cronstedtite-berthierine-amesite group, with a structure based on the two-layer sheets of the kaolin family, but presumably with a two-sheet repeat as compared with the three-sheet repeat of cronstedtite. It is also clear that the presence of a 14 Å. spacing is not necessarily evidence of a chlorite structure, but may be associated with a 'K-type' structure.

We propose for the new mineral the name *grovesite*, in honour of Dr. A. W. Groves, of the Mineral Resources Division of the Colonial Geological Surveys, who was geologist to the Home Ore Department, Iron and Steel Control, Ministry of Supply, during the war. Dr. Groves was responsible for the geological advice throughout the development and operation of this successful but sole Ministry of Supply manganese mine (1940–1946). During his periodic examination of the working he kept watch for unusual minerals, and it is due to him that the British Museum received the material in which the new minerals, banalsite, cymrite, pennantite, and now grovesite were discovered, along with others new to Great Britain.

[1] Chamosite (Berthier, 1820, originally from Chamoson, Switzerland) and berthierine (Beudant, 1832, originally from Hayanges, France) have long been supposed to be identical, but a variety of evidence recently accumulated (Bannister, Min. Mag. **25**–459; Orcel, Hénin, and Caillière, M.A. **11**-210; Orcel, Caillière, and Hénin, Min. Mag. **29**-331; Brindley, M.A. **11**–104 and Min. Mag. **29**–502) leads to the conclusion that they are distinct minerals. Chamosite is an oxidized chlorite (Min. Mag. **30**–279), while berthierine is structurally allied to cronstedtite, amesite, and the kaolin family. The names 'kaolin-type chamosite' and 'K-type chamosite' have been used as provisional names for berthierine before the true nature of the Hayanges mineral was established.

The determination of composition and thermal history of plagioclase by the X-ray powder method.

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[Read November 4, 1954.]

1. Introduction.

In a recent paper (hereafter referred to as GD) Goodyear and Duffin (1954) described X-ray powder data for a number of synthetic and chemically analysed plagioclases of composition An_0Ab_{100} $An_{100}Ab_0$. Important aspects of this work were a correlation of the X-ray patterns with chemical composition, and a distinction between the pattern of a naturally occurring material of low-temperature origin and that of a synthetic of similar composition. The investigation showed quite clearly that the unit-cell dimensions of a synthetic plagioclase depend but little on composition from An_0Ab_{100} to $An_{70}Ab_{30}$, whilst they differ from those of the low-temperature modification greatly for albite, to a lessening degree as the composition approaches $An_{70}Ab_{30}$, and practically not at all in the range $An_{70}Ab_{30}$–$An_{100}Ab_0$.

These features were studied quantitatively by plotting the angular separations, $\Delta 2\theta°$, of certain selected reflections in the X-ray pattern against composition, both for the natural and the synthetic materials. The resulting curves provided a possible means of estimating plagioclase composition from X-ray data: but it was evident that, without a sufficient knowledge of a specimen's thermal history, this method of analysis would be severely restricted. For instance, it seemed quite possible that the X-ray pattern of a partially inverted material, of composition within the range An_0Ab_{100}–$An_{70}Ab_{30}$, might be indistinguishable from that of a low-temperature modification of higher anorthite content.

The present work, described in the next section, has been undertaken to determine to what extent possible states of partial inversion lead to complications in determining plagioclase composition from X-ray data, and to establish whether or not the X-ray patterns of synthetics are identical with those of naturally occurring materials when fully inverted. The work of Tuttle and Bowen (1950) has shown that Amelia albite

when heated for 10 days at 1050° C. gives a pattern the same as that of synthetic albite, but they have not given corresponding data over the whole composition range An_0Ab_{100}–$An_{100}Ab_0$.

2. Experimental results.

Eight natural plagioclases were selected for heat-treatment from those described in detail in GD: the specimen numbers used in that paper have been retained here for easy reference (see table II). Since there is no clear distinction between X-ray patterns of synthetic and low-temperature materials of composition about $An_{70}Ab_{30}$, only materials of composition An_0Ab_{100}–$An_{65}Ab_{35}$ and $An_{80}Ab_{20}$–$An_{100}Ab_0$ have been studied. Specimen 15 is of volcanic origin and is probably partially inverted (see GD), while the remainder are almost certainly low-temperature modifications.

Each sample was heated at a prescribed temperature (controlled to ±10° C.) for a convenient length of time, after which it was cooled in air and examined by the X-ray powder method. All photographs were taken with filtered Co-$K\alpha$ radiation using a 20 cm.-diameter semi-focusing camera fitted with knife-edges for calibration purposes, the experimental arrangement being otherwise similar to that described in GD.

As preliminary experiments, samples of specimens 5 and 6 were heated for 2 days at 900° C. and 950° C. respectively and then at higher temperatures (for 2 days and at intervals of 50° C.) up to 1050° C., at which temperature significant changes were found to occur in the X-ray pattern. Both specimens were thereafter heated for varying lengths of time at still higher temperatures up to just below the melting point, the heating being continued at the final temperature until it was clear that the X-ray pattern was changing very little over a long period of time. With the changes occurring in specimens 5 and 6 as a guide, the specimens, 2, 4, and 7 were heat-treated similarly, commencing at 1050° C.

Specimen 14 was simply heated at 1400° C. for 2 days, and specimen 11 at 1350° C. for 3 days, while two separate samples of specimen 15 were taken, one being heated at 1400° C. for 2 days, and the other at 1100° C. for 4 days. This last treatment was an attempt to show that such 'annealing' leads to the production of a low-temperature form.

The main changes in the X-ray patterns due to heat-treatment are best described in terms of the angular separation of those reflections previously used (GD, table V); for convenience, descriptions of these

TABLE I. Descriptions of the reflections selected from the X-ray patterns.

Line.	Spacing (kX units).	Intensity.	Probable indices.
A	3·11–3·14	wm–ms	$2\bar{2}0$ or 220*
B	2·95–3·03	wm–ms	$1\bar{3}1$
C	2·63–2·65	wm–m	$\bar{1}32$
D	2·50–2·56	m–s	$24\bar{1}$
E	2·44–2·52	wm–s	$\bar{2}41$
F	1·825–1·833	m–ms	—
G	1·764–1·785	ms	—

* $2\bar{2}0$ for low-temperature albite.

TABLE II. Angular separations ($\Delta 2\theta^\circ$ for Cu-$K\alpha$ radiation) of the A–B, C–D, C–E and F–G reflections for heat-treated natural plagioclases.

Descriptions of specimens*								
Specimen No.	Composition wt. % An.	Heat-treatment.†				A–B.	C–D.	C–E.	F–G.
2	16·5	(i)	1050° C.	5	days	1·50	1·40	2·38	—
			+1100°	2	,,	1·43	1·52	2·35	—
		(f)	+1075°	21	,,	1·22	1·86	2·18	1·61
4	31·1	(i)	1050°	4	,,	1·26	1·67	2·18	—
		(f)	+1100°	7	,,	1·13	1·83	2·12	1·64
5	38·0	(i)	1050°	2	,,	1·23	1·70	2·14	—
			+1050°	2	,,	1·18	1·74	2·12	—
			+1075°	2	,,	1·15	1·83	2·09	—
		(f)	+1100°	7	,,	1·11	1·89	‡	1·70
6	51·6	(i)	1050°	2	,,	1·11	1·82	2·08	—
			+1050°	2	,,	1·09	1·83	2·07	—
			+1075°	2	,,	1·10	1·85	2·06	—
			+1100°	7	,,	1·08	1·87	‡	—
		(f)	+1150°	2	,,	1·07	1·91	‡	1·76
7	64·5	(i)	1050°	4	,,	1·05	1·87	‡	—
			+1100°	4	,,	1·07	1·90	‡	—
			+1150°	4	,,	1·07	1·92	‡	—
		(f)	+1200°	3	,,	1·07	1·91	‡	1·87
11	81·0		1350°	3	,,	—	—	—	1·98
14	93·0		1400°	2	,,	—	—	—	2·07
15	98·3		1400°	2	,,	—	—	—	2·09
	(volcanic)		1100°	4	,,	—	—	—	2·05

* Full descriptions of the specimens are given in GD, and the specimen numbers used in that paper are retained here.

† (i) and (f) indicate the initial and final stages of heat-treatment, values for which are plotted in Fig. 1. + indicates that the same sample was progressively heated.

‡ E reflection not sufficiently resolved from stronger D reflection for reliable measurement.

reflections are reproduced in table I. Table II gives the angular separations $\Delta 2\theta^\circ$ (calculated for Cu-$K\alpha$ radiation and accurate to within $\pm 0{\cdot}03^\circ$) of the A–B, C D, and C–E reflections at those stages of the treatment where significant changes were obtained, and of the F–G reflections for the final stage. Where no entry is to be found for the C E separation, the E reflection was no longer sufficiently resolved from the stronger D line for reliable measurements to be made. The column headed 'heat-treatment' gives temperatures and times of heating, a + sign indicating that the same sample was progressively heated.

3. Discussion.

It was clear from previous results (GD) that complications would arise in employing X-ray data for determining the composition of plagioclases with an anorthite content of 70–80 %. One of the features of the present work has been to examine the full potentialities of the X-ray method of analysis within the composition ranges An_0Ab_{100}–$An_{70}Ab_{30}$ and $An_{80}Ab_{20}$–$An_{100}Ab_0$, and consequently in discussing the new data in relation to the old it is desirable to consider each of these ranges separately.

(*a*) An_0Ab_{100}–$An_{70}Ab_{30}$.

Figs. 1 (i) and 1 (ii) show the relations based on previous data (GD) between compositions, from An_0Ab_{100} to $An_{70}Ab_{30}$, and the angular separations of the A–B, C D, and C–E reflections. These differ from those previously published (GD, figs. 4 and 5) only in that the curves for the natural materials are drawn to meet those of the synthetics at about $An_{70}Ab_{30}$. Included in the same figures are points corresponding to the initial and final stages of heat-treatment (table II) of specimens 2, 4, 5, 6, and 7.

It is clear that states of partial inversion are possible over the whole of this range, and it seems probable that the process of inversion is a continuous one, i.e. that any state between the low-temperature and high-temperature forms could be produced by appropriate heat-treatment. This greatly limits the assignment of a definite composition and thermal history to a plagioclase on the basis of its powder pattern, since the changes which take place as anorthite content increases are indeed found to be identical with those occurring on heat-treatment. An example of the ambiguity arising from this is afforded by specimen 2 (16·5 % anorthite), which after heating for 5 days at 1050° C. gives the same A–B, C–D, and C–E separations as a low-temperature oligoclase

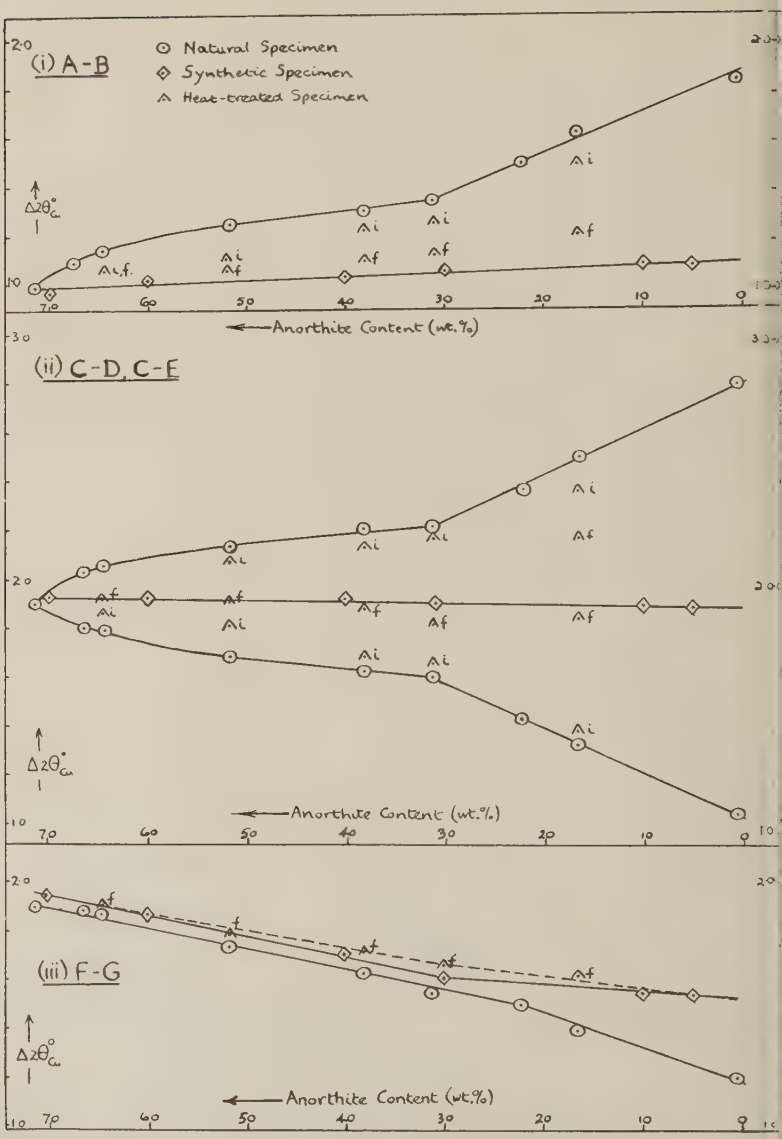

FIG. 1. Angular separation (calculated for Cu-$K\alpha$ radiation) of A–B, C–D, C–E and F–G reflections plotted against plagioclase composition for the range An_0Ab_{100}–$An_{70}Ab_{30}$. *i* = value after initial heat-treatment. *f* = value after final heat-treatment.

containing about 22 % anorthite; and quite clearly, in the absence of other information, the composition obtained by using figs. 1 (i) and 1 (ii) might have any value between 0 % and 22 % anorthite, depending on the state of inversion. It therefore seems that the use of these curves should be restricted as follows:

(i) A plagioclase known to be a low-temperature form from geological field data can be assigned a chemical composition as described previously (GD, section 5).

(ii) If the composition is known from chemical analysis, then the degree of inversion can be assessed from the values of the A–B, C–D, and C–E separations compared with the appropriate high- and low-temperature values (see 3 *c*, p. 655).

Further information might be obtained by using fig. 1 (iii) in which the angular separations of F–G reflections are plotted against composition from An_0Ab_{100} to $An_{70}Ab_{30}$. In this figure only the separations after the final stage of heat-treatment are added to the corresponding curves given in GD (fig. 6). Although the heat-treated specimens 2, 4, and 5 are not fully inverted according to their A–B and C–D separations, their F–G separations lie well above the synthetic curve. It has been mentioned previously (GD) that the synthetic materials of composition $An_{30}Ab_{70}$ $An_{60}Ab_{40}$ are poorly crystalline and give quite diffuse F reflections. Consequently values of their F–G separations might be in error more than the expected $\pm 0{\cdot}03^\circ$ in $\Delta 2\theta$. Further, since the F reflections of the natural materials remain well defined on heat-treatment, it is probable that a more appropriate high-temperature curve is represented by the dotted line shown in fig. 1 (iii).

Between 30 % and 70 % anorthite content, the F–G curves show that a composition can be estimated to ± 8 % anorthite irrespective of thermal history, and this information may be of value in limiting the ambiguity arising when only figs. 1 (i) and 1 (ii) are used. It should also be noted that if a specimen is known to be a high-temperature modification, the F–G curve still provides the only means of obtaining a reasonable estimate of composition between 30 % and 70 % anorthite.

It is now evident that, unless a specimen's thermal history is known, X-ray data alone cannot provide an accurate estimate of composition in the range An_0Ab_{100}–$An_{70}Ab_{30}$. In these circumstances the X-ray method is inferior to those based on optical data, since a combination of refractive-index measurements and a study of the orientation of the optical indicatrix with respect to the crystallographic axes enables

composition to be determined to ± 3 % anorthite over the whole range An_0Ab_{100}–$An_{100}Ab_0$ (I. D. Muir, private communication, 1954).

(*b*) $An_{80}Ab_{20}$–$An_{100}Ab_0$.

In this range the D and E reflections are either unresolved or are very close, and changes in their separation from the C reflection brought about by heat-treatment are small. For this reason, only the A–B and F–G separations can be reliably used, and these are plotted against composition in figs. 2 (i) and 2 (ii) respectively, in which the appropriate parts of figs. 4 and 6 in GD are reproduced, with values for heat-treated specimens added to fig. 2 (ii).

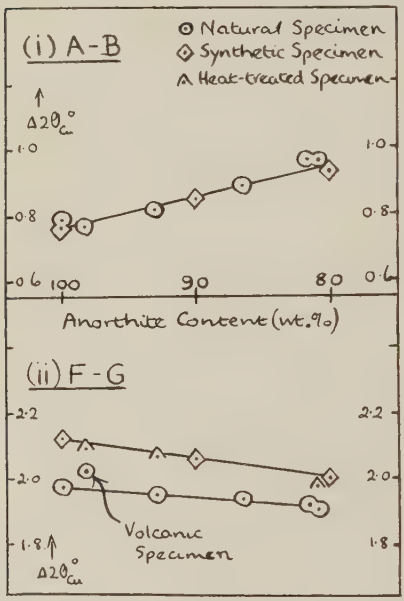

Fig. 2. Angular separation (calculated for Cu-$K\alpha$ radiation) of A–B and F–G reflections plotted against plagioclase composition for the range $An_{80}Ab_{20}$–$An_{100}Ab_0$.

The A–B separation permits the composition to be obtained, any difference between the high- and low-temperature curves being so small that thermal history does not affect the estimate. The degree of inversion is then given by the F–G separation, and although even here the difference between high- and low-temperature curves is not large, this method of distinction could be used with advantage in conjunction with that of Gay (1953), which employs a single-crystal diffraction technique.

Although the volcanic specimen 15 (98·3 % anorthite) appears to invert readily to the high-temperature form on heating for 2 days at 1400° C., 'annealing' at 1100° C. for 4 days failed to convert it to a true low-temperature form. It is interesting to note that treatment of a synthetic anorthite at 1100° C. for 3 days (see GD) succeeded only in reducing the F–G separation to a value similar to that of specimen 15. According to the work of Laves and Goldsmith (1954) synthetic anorthite is completely converted to the low-temperature form when heated at 1100° C., but in the case of a plagioclase of 98 % anorthite content

complete conversion is possible only at a lower temperature, confirming the present results for specimen 15.

(c) *General.*

Although most of the heat-treatments described here did not lead to complete identity of powder patterns of the natural materials with those of synthetic materials of the same composition, there seems no reason

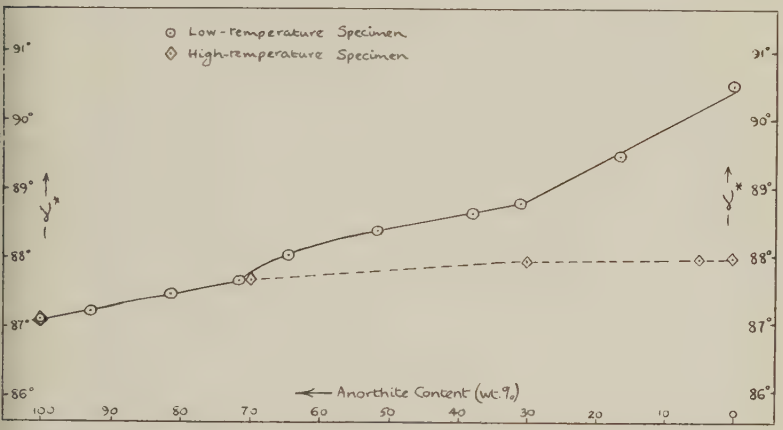

FIG. 3. The reciprocal-lattice parameter, γ^*, plotted against plagioclase composition.

to doubt that prolonged heating or, where possible, heating at temperatures rather higher than those employed in this work, would in fact produce this identity. Hence it may be safely assumed that the composition curves for the synthetics are those applicable for truly high-temperature modifications.

Calculations, based on previous X-ray powder data (GD, tables II and III), of reciprocal lattice parameters indicate that the changes which occur in the patterns of low-temperature plagioclases on increase of anorthite content, or on heat-treatment, are mainly due to a decrease in γ^* (see also Smith and Robbins, 1954). This is illustrated by the close similarity between the nature of the A–B, C–D, and C–E curves, and that of the variation of γ^* with composition shown in fig. 3, in which the values plotted are due to the authors, with the exception of those for synthetic albite (Donnay and Donnay, 1952) and natural anorthite (Cole, Sörum, and Taylor, 1951).

Although no distinction has been found between the parameters of

high- and low-temperature anorthites and bytownites, nevertheless it is clear that small differences must occur in view of the shifts of the higher order reflections (e.g. F and G) on heat-treatment. Corresponding movements of the lower-order reflections, which have been indexed (GD, tables II and III), are within the range of the experimental errors of the photographic technique used here, but they might very well be measurable using a high accuracy Geiger-counter spectrometer.

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The effect of isomorphous substitutions on the intensities of (00l) reflections of mica- and chlorite-type structures.

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Introduction.

A WIDELY used method of quantitative analysis in clay mineralogy is the comparison of the intensities of X-ray reflections from a so-called standard mineral with the unknown. In the clay minerals where isomorphous substitution is frequent the term 'mineral' generally covers a range of compositions and what is meant by such a term is a group of closely similar minerals. The so-called standard mineral is any member of a group which the particular worker may have in a pure or almost pure condition. If the standard mineral and the mineral in the unknown give different intensities for an equal volume of material the results will be inaccurate. It is therefore essential if we are to evaluate the standard-mineral method to see what sort of errors are involved in assuming all the members of a group have the same X-ray intensities. In this paper the effects of preferred orientation and absorption of X-rays in the specimen have been ignored, but, in a final analysis, these effects, too, would have to be taken into account.

The majority of clay minerals have layer structures and the different groups of clay minerals are readily characterized by their different layer thicknesses. In these layer structures the *a* and *b* axes are perpendicular and lie in the plane of the layers so the low order (00*l*) reflections are commonly used for both qualitative and quantitative mineralogical analysis. All the 2:1-type clay minerals either are, or can be converted into, mica-type and chlorite-type structures without alteration of the fundamental silicate layer. The montmorillonite and the vermiculite minerals, which can be regarded as expanded mica structures, can be collapsed by heating to give (00*l*) reflections in similar positions to the mica reflections. The intensities of the (00*l*) reflections from such heated specimens will depend on the nature and amount of the interlayer

material and on the constitution of the silicate layer as do those of the micas (see below). Thus calculations for mica-type and chlorite-type structures can be applied to the great majority of 2:1-type clay minerals.

Theory.

The intensity of a reflection from a fine powder (as defined by Brindley, 1945) recorded on a cylindrical film by the Debye-Scherrer method is given by

$$\frac{P}{I_0} = \frac{pl}{8\pi r \sin\theta} QVA\Psi, \qquad (1)$$

where P is the energy diffracted into length l of a Debye-Scherrer band by the set of planes (hkl), $(\bar{h}kl)$, and $(\bar{h}\bar{k}\bar{l})$ being considered as different sets. I_0 is the energy per unit area in the incident beam, r is the distance from specimen to film, p is the multiplicity factor for the set of planes considered, V is the volume of crystal powder irradiated of the substance giving the reflection, A is a factor for absorption in the specimen, Ψ is a factor for preferred orientation in the specimen.

$$Q = \frac{N^2\lambda^3}{\sin 2\theta} |F|^2 \left(\frac{e^2}{mc^2}\right)^2 \frac{1+\cos^2 2\theta}{2} \qquad (2)$$

where the symbols have their usual significance (James, 1950), in particular N is the number of unit cells per unit volume and F is the structure factor per unit cell. In the clay minerals a more appropriate unit is the unit layer and in this paper all F values are calculated for this unit and so N becomes the number of unit layers per unit volume.

For a given reflection from a given mineral group with a given λ equations (1) and (2) show that intensity is proportional to F^2. For clay mineral layer structures with a plane of symmetry parallel to the layers, if the origin of co-ordinates is taken at the plane of symmetry and the summation is made over half the unit layer, the expression for $F(00l)$ becomes

$$F(00l) = 2 \sum f_a \cos 2\pi l z, \qquad (3)$$

where f_a is the atomic scattering factor of atom type a for the radiation used and z is the fractional co-ordinate of the atom.

From equations (1), (2), and (3) it is apparent that within a mineral group the most important factor in changing low angle $(00l)$ intensities will be isomorphous substitutions, for atomic co-ordinates do not vary

nuch within a group and small variations in them do not affect the ntensities of low-angle reflections appreciably.

In the subsequent sections, tables of F values for basal reflections are given for micas and chlorites of different chemical compositions. The results are given as F's rather than in the form of intensities for a particular experimental method as F values can be converted to intensities for different experimental arrangements by using the appropriate equations (James, 1950).

Application to the mica group.

The clay minerals are composed of a framework of O and OH ions, the interstices of which may be filled with Si, Al, Mg, Fe, and K ions. Within a mineral group, if we treat O and OH together, the anion framework is constant and its scattering power for X-rays can be taken as that of the oxygens. Si, Al, and Mg have very similar atomic scattering factors (f_a's) at low angles of diffraction and this allows them to be treated together in a structural position where any two occur together, and in such cases the atomic scattering factor of the major occupant has been used for all such atoms in that position. For example, all tetrahedral atoms have been treated as Si, for Si is always the major occupant of these positions: in dioctahedral micas where the octahedral positions are largely filled with Al with slight replacement of Al by Mg and Fe, the atomic scattering factor for Al has been used for (Al, Mg), and the Fe atoms are treated separately.

In the mica structure we can have isomorphous substitution of Al for Si in tetrahedral positions, and Al, Mg, and Fe can all occur in octahedral positions. Of these the substitution of Fe is the only one which appreciably affects low-order (00l) intensities. The cation population of the interlayer position can also vary. There is less K in illites than in the true micas and it seems a fair assumption that the K-vacant positions in illites are occupied by H_2O or $(H_3O)^+$. If the K-vacant positions are indeed vacant in illites then the change in the intensities compared to true micas will be even greater than for a structure with H_2O or $(H_3O)^+$ in the interlayer positions, for the total scattering power of the atoms in the interlayer position will be changed even more.

Using the atomic co-ordinates given by Jackson and West (1930) for muscovite, the atomic scattering factors for atoms in silicates given by Bragg and West (1928), and taking the plane of the octahedral ions as origin, F(00l) per unit layer ($9\times5\times10$ Å. approximately) has been

calculated for reflections at 10 Å., 5 Å., and 3·3 Å. for dioctahedral micas whose composition lies within the limits,

$$K_2(Al,Si)_8(Al,Mg)_4O_{20}(OH)_4,$$
$$K_2(Al,Si)_8(Fe)_4O_{20}(OH)_4,$$
$$(H_2O)_2(Al,Si)_8(Al,Mg)_4O_{20}(OH)_4,$$
$$(H_2O)_2(Al,Si)_8(Fe_4)O_{20}(OH)_4.$$

A similar range is covered for trioctahedral micas.

TABLE I. Contributions of various parts of mica layer to the F's of $(00l)$ reflections

Section of structure.	Composition.	Contribution for $9\times5\times10$ Å.^{3}: F (10 Å.).	F (5 Å.).	F (3·3 Å.).
Skeleton	$(Si,Al)_8O_{20}(OH)_4$ (invariant)	17	$\overline{120}$	74
Interlayer	2·0 K —	$\overline{37}$	34	$\overline{30}$
	1·5 K 0·5 H_2O	$\overline{32}$	30	$\overline{26}$
	1·0 K 1·0 H_2O	$\overline{27}$	25	$\overline{22}$
	0·5 K 1·5 H_2O	$\overline{23}$	21	$\overline{18}$
	— 2·0 H_2O	$\overline{18}$	16	$\overline{14}$

Octahedral		Normal.	Anomalous.	Normal.	Anomalous.	Normal.	Anomalous.
4Al	...	45	45	42	42	39	39
3Al1Fe	...	58	54	54	51	50	46
2Al2Fe	...	71	64	66	59	60	52
1Al3Fe	...	85	73	78	67	71	59
4Fe	...	98	82	90	75	81	66
6Mg	...	68	68	62	62	56	56
5Mg1Fe	...	81	78	75	71	67	63
4Mg2Fe	...	94	87	87	79	78	70
3Mg3Fe	...	107	96	99	87	89	77
2Mg4Fe	...	120	105	111	96	100	84
1Mg5Fe	...	133	114	123	104	111	91
6Fe	...	146	123	136	112	122	98

The results are in table I. They are given as contributions of various parts of the mica structure to $F(00l)$ per unit layer. The invariant skeleton consists of the tetrahedral cations and the oxygen framework. The interlayer and the octahedral contributions are given for different atomic populations of these positions. The octahedral contributions are given under two headings, normal and anomalous. This is necessary because the atomic scattering factor of Fe is reduced when Co-$K\alpha$ radiation is used owing to anomalous dispersion. The F value for any basal reflection of a particular mica is given by the sum of the appropriate contributions obtained from table I.

For example, for the 5 Å. reflection from a mica of composition $(K_{1\cdot5}(H_2O)_{0\cdot5})(Al_3Fe_1)(Al,Si)_8O_{20}(OH)_4$:

(*a*) with Cu-$K\alpha$ radiation

$$F(5) = F(5)(\text{skeleton}) + F(5)(Al_3Fe_1) + F(5)(K_{1\cdot5}(H_2O)_{0\cdot5})$$
$$= \overline{120}+54+30 = \overline{36};$$

(*b*) with Co-$K\alpha$ radiation

$$F(5) = \overline{120}+51+30 = \overline{39}.$$

For compositions intermediate between those given in table I interpolation gives accurate values for F.

Application to the chlorite group.

For the calculations on this group the same curves of atomic scattering factor were used as before and corrections for anomalous dispersion of Co-$K\alpha$ radiation by Fe were made. The atomic co-ordinates used were those given by Norrish (1952) which are closely similar to those given by Brindley and Robinson (1951). The plane of the mica layer octahedral cation sheet which is a symmetry plane was taken as the origin of co-ordinates.

The chlorite structure consists of a regular interleaving of mica-type and brucite-type layers. There are therefore two kinds of octahedral sites per unit layer and in both of these Fe may replace (Mg,Al). The calculations in this paper deal only with chlorites where both octahedral layers are trioctahedral. The replacement of (Mg,Al) by Fe is the only isomorphous replacement commonly encountered which would change the intensities of the low-order basal reflections. For a given Fe content the octahedral atoms can be arranged in different ways between the two types of octahedral site so both number and arrangement of Fe atoms affect intensities.

The F values per unit layer for (00l) reflections at 14 Å., 7 Å., 4·7 Å., and 3·5 Å. have been calculated for chlorites whose chemical composition lies in the range

$$[(Mg,Al)_{12}][(Si,Al)_8]O_{20}(OH)_{16}$$

and

$$[(Mg,Al)_4Fe_8][(Si,Al)_8]O_{20}(OH)_{16}$$

for both symmetrical and asymmetrical arrangements of the octahedral ions.

For chlorite structures the intensities of the basal reflections at 7 Å. and 3·5 Å. are dependent on the Fe content but independent of its

arrangement. Values for $F(7)$ and $F(3{\cdot}5)$ are given in table II for the range of chemical composition previously indicated at intervals of 1 F

TABLE II. F (7 Å.) and F (3·5 Å.) for (00l) reflections of chlorite-type structures for a unit layer.

Octahedral atoms (per unit layer).	F (7 Å.)		F (3·5 Å.)	
	Normal.	Anomalous.	Normal.	Anomalous.
12Mg	95	95	150	150
11Mg1Fe...	108	104	161	157
10Mg2Fe...	120	113	172	165
9Mg3Fe	133	122	184	172
8Mg4Fe	146	130	195	179
7Mg5Fe	159	139	206	186
6Mg6Fe	172	148	217	193
5Mg7Fe	184	157	228	201
4Mg8Fe	197	166	239	208

atom per unit layer. The F's for basal reflections at 14 Å. and 4·7 Å. depend on the difference in scattering power between the occupants of the two types of octahedral sites. Table III gives the values for $F(14$

TABLE III. F (14 Å.) and F (4·7 Å.) for (00l) reflections of chlorite-type structures for a unit layer.

Content of mica octahedral sheet less content of brucite octahedral sheet.	F (14 Å.)		F (4·7 Å.)	
	Normal.	Anomalous.	Normal.	Anomalous.
6Mg–6Fe...	$\overline{29}$	$\overline{29}$	$\overline{196}$	$\overline{196}$
5Mg–5Fe...	$\overline{16}$	$\overline{18}$	$\overline{184}$	$\overline{188}$
4Mg–4Fe...	$\overline{2}$	$\overline{6}$	$\overline{172}$	$\overline{180}$
3Mg–3Fe...	11	5	$\overline{160}$	$\overline{172}$
2Mg–2Fe...	24	17	$\overline{148}$	$\overline{164}$
1Mg–1Fe...	38	28	$\overline{136}$	$\overline{156}$
0Mg–0Fe...	51	40	$\overline{124}$	$\overline{147}$
1Fe–1Mg...	65	51	$\overline{112}$	$\overline{139}$
2Fe–2Mg...	78	63	$\overline{100}$	$\overline{131}$
3Fe–3Mg...	91	74	$\overline{88}$	$\overline{123}$
4Fe–4Mg...	105	86	$\overline{76}$	$\overline{115}$
5Fe–5Mg...	118	97	$\overline{64}$	$\overline{107}$
6Fe–6Mg...	132	109	$\overline{52}$	$\overline{99}$

and $F(4{\cdot}7)$ for the possible differences in scattering power between the two types of site, the difference in scattering power being reckoned as mica octahedral contribution less brucite octahedral contribution.

To obtain the F values for a chlorite of a particular composition, the $F(7)$ and $F(3{\cdot}5)$ values are obtained from table II. There are usually several possible arrangements of the octahedral atoms and so several

possible values for $F(14)$ and $F(4{\cdot}7)$ can be obtained from table III corresponding to the possible arrangements.

For example, to obtain the F values for a chlorite (for Cu-$K\alpha$) which contains 2 Fe atoms per unit layer, i.e. $[(Mg,Al)_{10}Fe_2][(Al,Si)_8]O_{20}(OH)_{16}$, from table III $F(7) = 120$ and $F(3{\cdot}5) = 172$. With 2 Fe atoms per unit layer the possible $F(14)$ and $F(4{\cdot}7)$ are obtained as shown in table IV.

TABLE IV. Possible F (14 Å.) and F (4·7 Å.) values for $(00l)$ reflections of a chlorite structure of composition $(Mg_{10}Fe_2)(SiAl)_8O_{20}(OH)_{16}$ per unit layer.

Possible arrangements.			From table III.	
Mica.	Brucite.	Difference.	F (14 Å.)	F (4·7 Å.)
6Mg	4Mg,2Fe	2Mg–2Fe	24	$\overline{148}$
5Mg,1Fe	5Mg,1Fe	0Mg–0Fe	51	$\overline{124}$
4Mg,2Fe	6Mg	2Fe–2Mg	78	$\overline{100}$

The converse of the above method can also be applied. From the ratio $F(7)/F(3{\cdot}5)$ the Fe content of a chlorite can be obtained and from the ratio $F(14)/F(4{\cdot}7)$ it may be possible to decide how the atoms are arranged.

Discussion.

There are four points which should be brought to notice:

(1) If the intensities of an unknown mica or chlorite after correction for absorption, orientation, &c., do not fit the calculated data, then either its chemical composition lies outside the range for which calculations have been made or the atomic co-ordinates are significantly different from those used here and the reason for the discrepancy should first be sought in them.

(2) F values for micas and chlorites apply to the stated unit volumes and therefore their F's are not directly comparable.

(3) In connexion with quantitative analysis by the standard-mineral method the data in tables II, III, and IV show that appreciable changes in F and hence in intensities occur in both micas and chlorites owing to isomorphous substitution. This effect is illustrated in table V, which gives the relative intensities of Debye-Scherrer reflections with Cu-$K\alpha$

TABLE V. Relative intensities of $(00l)$ reflections for equal volumes of different mica-type minerals.

		Relative intensities of $(00l)$ reflections.		
Mineral.	Structural formula.	10 Å.	5 Å.	3·3 Å.
Muscovite	$K_2(Al_4)(Si,Al)_8O_{20}(OH)_4$	1·0	0·7	1·2
Phlogopite	$K_2(Mg_6)(Si,Al)_8O_{20}(OH)_4$	3·6	0·2	1·7
Illite	$K_1(H_2O)_1(Al_4)(Si,Al)_8O_{20}(OH)_4$	1·9	1·0	1·4

for equal volumes of three minerals of mica structural type (ide formulae). The results show that large errors can occur in the standa mineral method unless great care is taken to match the standard miner and the mineral in the unknown. It is also of interest that the integra intensity of the 10 Å. reflection from an illite should be greater than th of muscovite if the illite specimen is totally composed of crystall material.

(4) The calculations suggest a possible alternative to the standa mineral method of quantitative analysis. For this the preferred orien tion factor Υ, the absorption factor A, and the relative integra intensities have to be measured for (00l) reflections. This invol extra work but in the standard-mineral method A and Υ are usua ignored, the assumption being that both factors are the same in th standard and the unknown or that the factors are negligible, and it further assumed that peak intensities are proportional to integrate intensities in both the standard and the unknown. There is no grea difficulty in evaluating all of these. The absorption factor can be calc lated from the chemical composition of the unknown mixture, the pre ferred orientation of the specimen can be measured in several ways (e.g Brindley, 1953), and the relative integrated intensities can be obtaine by detailed photometry of line profiles or more directly using diffracto meters.

The problem of finding the percentage of mica (say) in a mixture con sists in evaluating equation (1) for V_{mica}. Assuming absorption an preferred orientation factors have already been obtained, the unknow factors in equation (1) applied to mica reflections are P/I_0, F^2, and V_{mica}.

(i) To obtain the F^2 values for the particular mica in the mixture.—I the absolute intensities of the (00l) reflections, say 1, 2, 3, &c., of the mic in the unknown are P_1/I_0, P_2/I_0, P_3/I_0, &c., then their integrated relativ intensities on a Debye-Scherrer powder pattern are P_1, P_2, P_3, &c.

From equation (1)

$$\frac{P_1}{P_2} = \frac{F_1^2 \Upsilon_1 A_1 \Xi_1}{F_2^2 \Upsilon_2 A_2 \Xi_2}, \qquad (4$$

where Ξ is the combined cone size and polarization factor for a randomly oriented powder and is equal to

$$\frac{1+\cos^2 2\theta}{\sin^2\theta \cos\theta}$$

and Υ, A, F, and P have the same meaning as in equation (1). From the photograph we obtain the ratios P_1/P_2, P_2/P_3, &c., and Υ_1, Υ_2, A_1, A_2

Ξ_1, Ξ_2 can all be obtained. Hence using equation (4) we obtain the ratio F_1^2/F_2^2 and similarly F_2^2/F_3^2, &c. Consideration of the (060) spacing of the mica along with the best fit of observed and calculated values of the ratios F_1^2/F_2^2, &c., gives the F^2 values of the particular mica in the mixture.

(ii) To obtain P/I_0.—P/I_0 is the absolute intensity of a reflection. With photographic methods, to evaluate P/I_0 a known volume of an internal standard,[1] e.g. sodium chloride whose absolute intensities are known, is mixed with the unknown powder. Comparison of the integrated relative intensities of the sodium chloride reflections with their known absolute intensities gives the factor to apply to the integrated relative intensities of the mica reflections to put them on an absolute scale. With spectrometers absolute intensities can be determined directly without using an internal standard by monitoring both incident and reflected beams.

Having obtained two of the three unknowns in equation (1) substitution gives V_{mica}, and the proportion of mica in the mixture can then be obtained.

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[1] Care must be taken that both the unknown and the internal standard satisfy the conditions specified by Brindley (1945) for a fine powder.

Projector for interference figures and for direct measurement of 2V.

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THE instrument is designed for the study and measurement of t optical characters of crystals and anisotropic materials. The con scopic phenomena, over a wide area for any selected orientation of th specimen, may be brought into view on a hemispherical screen, withou the use of a microscope or lens system. The parts of the interferenc figure retain their true angular relationships, directly displaying fo observation or measurement values of 2V for any angular separation o the optic axes.

The polarizing microscope has certain limitations; for example, obser vations, usually monocular, can be made only by one person at a tim and errors of interpretation may arise. The fixed position of the crysta in its mount allows no change or choice of orientation. In addition, th significant area of the figure is restricted, not only by the lens system but also because the apparent angle in air, 2E and not 2V, is observed so that only a minor portion of the convergent phenomena is visible i the field of view of the microscope, and only small optic axial angl separations may be observed. The microscope projector has the singl advantage that the figure may be viewed on a flat screen by a group o observers using normal vision. However, this equipment is elaborat and unsuitable for individual studies and measurements. The optic axia goniometer and the universal stage are available for quantitative work but special techniques restrict their use. T. T. Quirke[1] has describe methods for projection and measurement, using a converging len system and crystal sections with fixed orientation. The procedure i based on the apparent axial angle (2E), giving a limited effective field and is therefore applicable to crystals with small axial angles. H. Win

[1] T. T. Quirke, Direct projection of optic figures. Amer. Min., 1938, vol. 23 pp. 595–605. [M.A. 7–249.]

chell[1] describes the use of cut spheres made of crystals such as corundum or quartz, for demonstration of optic figures when manipulated between polaroid sheets. The interference figure may be viewed inside the sphere and projection can be arranged. Quite recently, C. S. Hurlbut, by placing a glass (or plastic) sphere above the crystal section, shows the interference figure reflected in a mirror.[2]

In the method here described, the crystal, mounted at the centre of a transparent sphere, is capable of free revolution about its centre, and is illuminated by polarized light converging upon it at a wide angle from a reflector. The emergent rays traverse the analyser, and combine to produce a focused image of the interference figure on the spherical surface of the screen. The curvature and position of the screen are so arranged that the sphere and screen are concentric when the interference figure is in focus over the whole of the screen. The phenomena may be examined while the sphere is revolved, giving in effect a working model of the crystal and its indicatrix for any desired orientation. Two optic axes may be seen at one time on the screen, for an angular separation of up to 120 degrees, so that the true optic axial angle, 2V acute, of any magnitude may be directly measured upon the screen. Simple in use and construction, the instrument is suitable for both class demonstration and individual operation; and, when the dimensions of the screen and its positioning are correctly arranged, accurate and reliable values for optic angles are directly measurable for crystal grains or plates of a diameter of two mm. and upwards. By removal of the screen, and also the sphere when necessary, and reduction of the light aperture, the instrument is converted to a parallel light polariscope.

The apparatus is shown, as a partially diagrammatic sectional view, in fig. 1. The overall dimensions there illustrated are adequate for much larger sphere and screen. The sphere, A, is constructed of two equal segments of glass.[3] Each segment has, cemented to its plane surface, a metal ring, the ring on one segment being an accurate fit within that on the other, and the dimensions are such that, when assembled, the segments are separated by a narrow space to accommodate the crystal, and externally form a sphere, with the outer metal ring forming part of the surface.

[1] H. Winchell, Demonstration of interference figures. Amer. Min., 1947, vol. 32, pp. 588–589. [M.A. **10**–468.]

[2] C. S. Hurlbut, Jr., Demonstration polariscope. Amer. Min., 1955, vol. 40, pp. 120–122.

[3] H. C. G. Vincent, Min. Mag., 1954, vol. 30, p. 513.

The sphere is supported in the central opening of the circular metal stage, B, which rotates in a recess in the cover, C, of the reflector. The opening has three equally spaced hardened steel balls, D, let into its

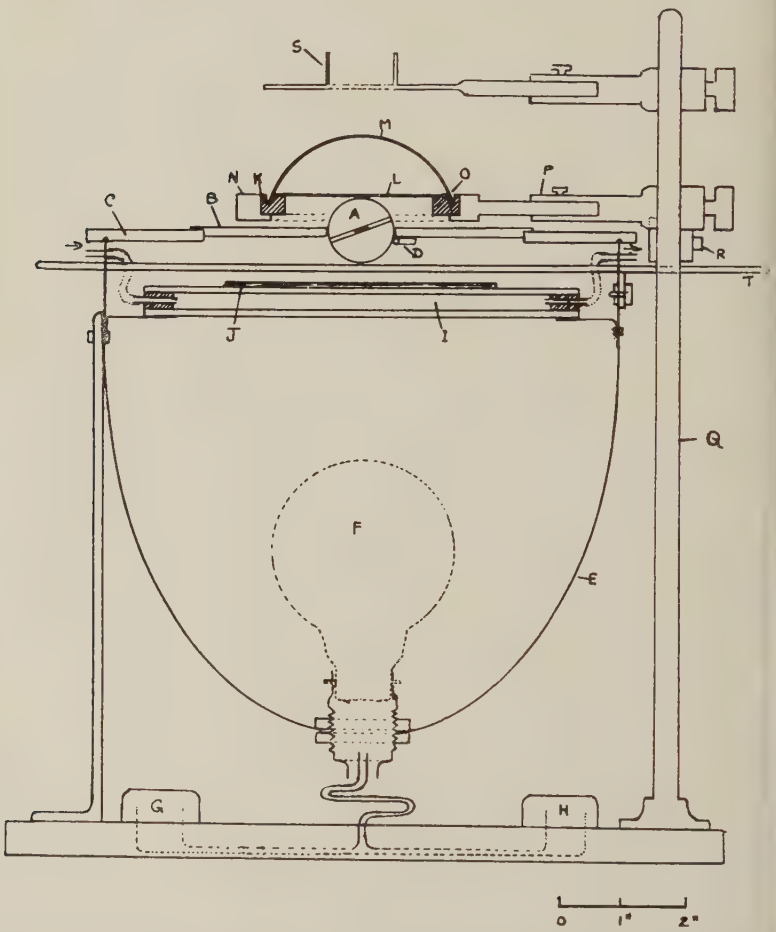

FIG. 1. Projection apparatus in convergent light. A sphere, B stage, C cover, D ball supports, E reflector, F lamp, G switch, H plug, I water cell, J polarizer, K inner ring, L analyser, M viewing screen, N outer ring, O groove, P horizontal arm, Q post, R adjustable stop, S masking tube, T strip.

circumference, and adjustable in position. The sphere revolves freely on this three-point support and the small clearance between the sphere and the plate may be screened by a ring of black velvet.

The cover carrying the stage and sphere fits over the circular edge of the reflector, E. The shape of the reflector is not critical, but should be chosen to give a strong concentration of light on the sphere over a wide angle, and the light bulb, F, should be adjustable in height. Illumination is conveniently provided by standard lamps on the mains supply. The reflector carries the water cell, I, the surface of which is preferably of 'perspex' or similar plastic, sanded to diffuse the light from below. The cell, fed slowly from a convenient supply, effectively absorbs the heat and allows continuous operation even when high consumption lamps are in use.

A circular sheet of polaroid, the polarizer, J, rests upon the upper surface of the cell and is of adequate diameter to allow the maximum angle for the cone of rays entering the sphere.

The projection screen and upper polaroid assembly is supported axially above the sphere, and consists of an inner metal ring, K, carrying the polaroid analyser, L, and the screen, M, which is free to rotate in an outer ring, N. The screen may be made from an accurately blown spherical ground-glass bulb of the proper diameter. Its radius of curvature should be equal to the distance from the centre of the sphere to the focal position of the interference figure. The position may be found by trial, using the optic axial figure of a thick flake of muscovite mounted in the sphere, focused on the upper surface of a sheet of ground-glass held above. The inner ring, K, has a shallow circular groove, O, in which the screen fits. Ring and screen may each be independently rotated. The disk of polaroid, L, is fitted into the central opening, which is maintained as large as the screen will allow. The screen assembly is supported by a stout horizontal arm, P, adjustable in length, which slides up and down along the rigid vertical post, Q, firmly attached to the base of the instrument. An adjustable stop, R, on the post fixes the correct height and position for the screen, at which point its surface is truly concentric with that of the sphere, and the screen assembly may also be swung to one side.

The relative positions indicated are designed to give the maximum effective area for the projection screen, allowing it to display, for one given orientation of the crystal, both optic axes with an angular separation of up to about 120 degrees, with associated indicatrix phenomena, over an area of about two-thirds of a hemisphere.

The masking tube, S, may be swung into position to limit the interference figure visible to a small area comparable to that seen in a polarizing microscope, and is useful in teaching.

A 'perspex' or glass strip, T, operates through horizontal slots on opposite sides of the reflector and is adjustable in height so that the sphere rests upon it and the weight of the sphere is partially taken by the strip. Thus, by moving the strip in any desired direction in its horizontal plane, the sphere may be revolved on any axis in order to vary the orientation of the crystal while the screen is under observation. The instrument should be well ventilated and necessary parts rendered dull black or screened. If the instrument is not intended for accurate measurement, sphere and screen may be made of 'perspex' or similar plastic.

Projection is best when the area of the crystal is relatively large, and the retardation moderate or high. Crystals as plates, cut sections, or grains, are mounted between cover-slip glass in a solid or liquid medium in optical continuity with the sphere. The refractive index of the embedding medium should preferably be near that of β for the crystal; and, to avoid total reflection effects, it may be advisable to use mounting materials with indices near or higher than that of the sphere. If necessary, special cover-slips may be ground for the purpose from high refractive index glass.

Of the rays entering the sphere, those which do not pass through the crystal may give a background of undesirable illumination on the screen, and so reduce the quality of the image. They may be eliminated when necessary by means of a mask of foil, with a central opening, attached to one of the segments.

The instrument is best used in a darkened room. After adjusting the light source for the most effective concentration, the inner ring is rotated to extinction, and the sphere, with the crystal mounted at the centre, is placed in its support. Specimens give the best results when the plane of separation of the segments is not too highly tilted and when the acute bisectrix, or an optic axis, is highly inclined to this plane. Stray illumination on one side of the screen arising when the orientation of the specimen is unfavourable should be screened off near the sphere. Utilizing the transparent strip, T, the sphere may be revolved to display the interference phenomena for any desired crystal orientation.

The crystal may also be revolved by turning the stage, and both analyser and screen have independent rotation. The behaviour of the isogyres, and other conoscopic phenomena, may therefore be observed and demonstrated for any chosen orientation. The interference figure of a thick flake of muscovite, 2V 43°, is shown in fig. 2.

The optic axial angle is afforded directly by the great circle measure-

ment on the screen between the two optic axes, which may be adjusted to fall upon the scale of degrees inscribed in the screen; or a strip of metal, fitting the curve of the screen and marked in degrees, may be used enabling measurements to be made at any position. The principal planes and points of emergence of the axes of the indicatrix are also available and may be temporarily inscribed on the screen if desired.

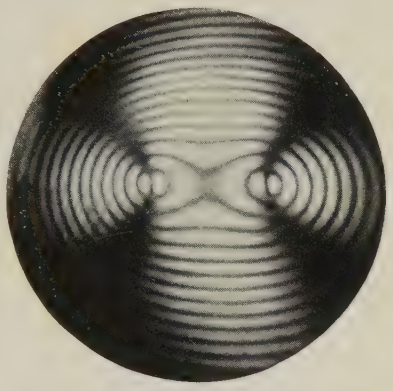

Fig. 2. Interference figure of muscovite.

When the refractive index of the glass comprising the sphere differs from that of β of the crystal, correction of the observed value of 2V is necessary. If β for the crystal is known, and also the great circle measurement from each optic axis to the polar point of emergence on the screen of the axis of the sphere perpendicular to the plane of separation of the segments, the true value for 2V is readily available. The two opposite polar points having been marked on the sphere, the equivalent screen-point may be located and established, utilizing a drop of benzine held by surface tension against the surface of the screen by means of a glass slide. This acts as a lens and also renders the screen temporarily transparent, enabling the polar points on the sphere to be aligned and the equivalent point inscribed on the screen. By reference to a chart the amended angular readings are available and may be marked off from the polar point, thus giving each corrected optic axis position for measurement of 2V. To improve accuracy in quantitative work the sphere may be reversed to obtain the mean of two sets of readings.

For studies in parallel polarized light the screen is removed and the illumination restricted to a small aperture at the centre of a disk placed upon the cell. Becke-line observations are made with a hand-lens for refractive index determination.

When monochromatic light is required, the sphere may be illuminated by a sodium-vapour lamp or other source inserted in an opening for the purpose in the side of the reflector and dyed photographic plates are useful as filters for demonstration work.

The hydration of larnite (β-Ca_2SiO_4) and bredigite (α_1-Ca_2SiO_4) and the properties of the resulting gelatinous mineral plombierite.

(With Plate XVII.)

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[Read November 4, 1954.]

Introduction.

In this paper the formation of a gelatinous hydrate phase from the natural dicalcium silicate minerals larnite and bredigite is described. Detailed study of the gel so formed indicates that the process of hydration is a solid reaction which is effected by diffusion. The preferred orientation of the hydrate phase suggests that the hydration is facilitated by a relationship between the structure of the anhydrous silicate and that of the hydrate phase produced.

In this investigation the variations in density, mean refractive index, and chemical composition of the natural gels have been determined and the characteristics of the adsorbed water studied by isothermal dehydration and rehydration. In discussing the mechanism of hydration it has been assumed that this obtains at constant volume. This assumption is based on the study of gel pseudomorphs after single crystals of larnite and bredigite in thin section.

The orientation of the hydrate phase relative to the original crystallographic directions of the parent silicate has been determined from single-crystal X-ray photographs of gel pseudomorphs after bredigite.

The hydration mechanism, as deduced from the experimental evidence presented below, is thought to have considerable bearing on the hydration reactions of β-Ca_2SiO_4, and of gel formation from this compound, in the hydration of portland cement clinker.

Occurrence.

The gels examined during the present investigation were collected at the dolerite-chalk contacts at Ballycraigy and Scawt Hill, both of which

are near Larne, County Antrim. In a previous paper the natural gel from Ballycraigy was briefly described, and identified with the mineral plombierite and also with a synthetic preparation 'calcium silicate hydrate (I)' (McConnell, 1954, p. 302). The gels have been formed through the hydration, under natural conditions, of the minerals larnite and bredigite. Accounts of the occurrence of these minerals at the Scawt Hill contact have been given by Tilley (1929, p. 77; 1948, p. 257). An account of the dolerite-chalk contact at Ballycraigy is in course of preparation.

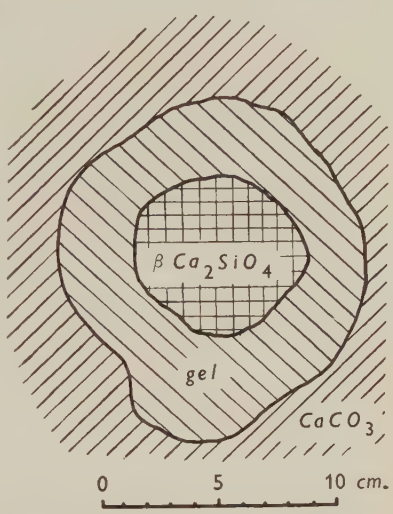

Fig. 1. Diagrammatic section through a metasomatized flint nodule from Scawt Hill, Co. Antrim.

Larnite rocks occur in the endogenous zones at both contacts. At Scawt Hill they have been formed through the magmatic silicification of the chalk rock at the immediate contact, and also through the metasomatic reaction of flint nodules with the surrounding chalk at a distance of several feet from the contact. The larnite nodules formed in the latter instance are extremely pure and are invariably surrounded by a sheath of gelatinized larnite up to five centimetres in radial thickness. A diagrammatic section through one such nodule is shown in fig. 1. The gel sheath is homogeneous and has an extremely sharp contact with the unhydrated larnite core. The outer contact between the gel and the recrystallized chalk is less well defined and appears to represent the original boundary of the flint nodule.

The gel is a transparent to translucent solid. It is brittle and breaks with a conchoidal fracture. In colour it ranges from pink to red-brown and its hardness is approximately 4.

Refractive index and density determinations.

The natural gel has a birefringence varying between 0·001 and 0·003. In any sample from a single location at the contact a small range in refractive index was observed in the crushed material. On such a sample

a mean refractive index could be determined, and in samples from different locations at the contact a considerable range in the mean refractive index, thus defined, was observed. In fig. 2 the mean refractive indices of a series of samples have been plotted against their density, as determined by suspension in liquid. This plot illustrates a linear relationship between the mean refractive index of the gel and its density. The total variation in the latter corresponds to a factor of 10% approximately. Later in the present paper chemical analyses of two of these gel samples are compared (samples A and B on fig. 2). The comparison indicates that density variation is not, in the main, a function of variable chemical composition. The graph presented approximates to the classical equation,

$$(\mu-1)/\rho = K_G,$$

given by Gladstone and Dale, where μ is the refractive index, ρ the density, and K_G a constant. From this relationship it is evident that the gel behaves optically in a manner analogous to compressible liquids.

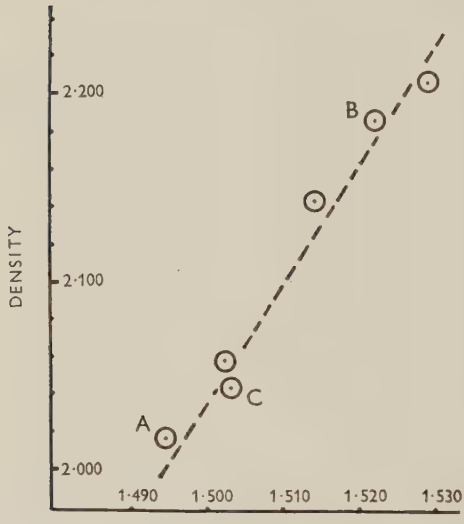

FIG. 2. Plot of density against mean refractive index for a series of gel samples. Points A, B, and C correspond to analyses A, B, and C in table I.

THIN-SECTION STUDY OF THE GEL AND THE REPLACEMENT PROCESS.

In thin section the gel is seen to pseudomorph both larnite and bredigite. The pseudomorphs have low birefringence and moderately sharp extinction. In suitably orientated sections pseudomorphs after bredigite yield a perfect biaxial interference figure; 2V being positive and equal to that of the parent silicate. Examination of a number of partly hydrated bredigite crystals by means of the Berek compensator indicated that the birefringence of the bredigite was reduced by a factor of five on gelatinization, regardless of the orientation of the original section.

The formation of gel pseudomorphs after larnite in a larnite-spinel-ock from Ballycraigy is illustrated in pl. XVII, and the relationships etween the several zones present are shown on the overlay over fig. 1. 'he hydration interface between the larnite and gel is sharp and crosses ndividual crystals without respect to their orientation, and no preferen-ial hydration along grain boundaries was observed in this or other ections. Under crossed nicols relict lamellar twinning can be seen n crystals marked L, alternate lamellae extinguishing together. Examination of a large number of thin sections suggests that the hydra-ion process is effected without appreciable volume change.

X-ray examination.

X-ray powder data for the gel have been presented previously McConnell, 1954, p. 297). During the present study powder photographs f material representing the limits in density variation were compared nd found to be identical.

A single crystal of bredigite, pseudomorphed by gel, was examined by ingle-crystal X-ray techniques. The original crystallographic directions f the bredigite were determined from an optical examination of the seudomorph. The single-crystal photographs showed that the reflec-ions given by the pseudomorph were orientated and these were subse-uently indexed, indicating that the b^* direction of the hydrate phase vas orientated parallel to the c^* direction of the parent bredigite Douglas, 1952, p. 878), and that the a^* direction of the hydrate was andomly orientated in the plane normal to this direction. The existence f preferred orientation in the hydrate phase suggests that the original tructure of the bredigite is inherited to some degree.

Chemical composition and dehydration of the gel.

An analysis of plombierite from Ballycraigy has already been given McConnell, 1954, p. 302) and this is shown together with a second analy-is in table I. In an earlier section it has been noted that the chemical omposition of the gel is sensibly independent of variation in the density f the gel. The third analysis in table I was carried out on a larger ample of the gel collected from a hydrated larnite nodule at Scawt Hill.

Part of the last sample was used for the adsorption experiments now o be described. The apparatus used for these experiments was ex-remely simple: 100 mg. samples of the gel, graded between 90 and 150 esh, were placed in a shallow boat and suspended on a helical glass pring in a vertically mounted cylindrical desiccator. Movement of the

TABLE I. Chemical analyses of plombierite gels from Ballycraigy and Scawt Hill, Co. Antrim.

	A.	B.	C.	C_1.	C_2.
SiO_2	40·4	39·9	41·76	6·00	5·96
Al_2O_3	2·4	4·3	0·23	...	...
Fe_2O_3	0·8	0·5	0·47	...	...
MgO	0·3	0·0	0·30	...	...
CaO	32·6	31·9	31·18	4·80	4·76
Na_2O	n.d.	n.d.	0·18	...	...
K_2O	n.d.	n.d.	0·10	...	...
TiO_2	n.d.	n.d.	0·20	...	...
Mn_2O_3	n.d.	n.d.	0·05	...	...
H_2O- (110°)	23·3	23·0	14·76	...	...
H_2O+ (1000°)			10·72	...	...
	99·8	99·6	99·95	...	...
Density	2·018	2·186	2·042	...	...
Mean ref. ind.	1·495	1·523	1·503	...	...

A. Natural gel from Ballycraigy. (McConnell, 1954, p. 302.)

B. Ditto. New analysis by author on 0·30 gm.

C. Gel from Scawt Hill. Analyst, L. J. Larner, Building Research Station, Garston, Herts.

C_1. Molecular ratios $CaO:SiO_2$ on basis $6SiO_2$ from analysis C.

C_2. Number of silicon and calcium atoms in the volumetrical equivalent of half the unit cell of bredigite from the same sample of material.

spring with respect to a fixed reference point, coaxial with the desiccator, was measured by means of a travelling microscope. The method allowed of the determination of weight change of the order of 0·05 % of the total weight of the gel sample. In practice the desiccator was permanently evacuated and sulphuric acid solutions of known concentration were introduced, in turn, and time-weight loss curves plotted for the gel sample. From these curves the relative rates of diffusion at different vapour pressures, and the final degree of approach to equilibrium, were estimated. The diffusion coefficient was found to decrease rapidly with decreasing vapour pressure and at low vapour pressures near equilibrium was attained only after a period of weeks.

Two different experiments were carried out. In the first of these the sample was dehydrated from 80 % relative humidity to near zero humidity and then rehydrated. In the second experiment dehydration was taken to 15 % relative humidity and the sample rehydrated from this point. Different samples were used in each experiment. The adsorption curves are given in fig. 3 and the most important features shown by them are listed below:

1. A marked break in the desorption curves occurs at 40 % relative humidity.

2. Rehydration after complete dehydration is accompanied by marked hysteresis.
3. Dehydration and rehydration between the limits of 40 and 15 % relative humidity appear to be strictly reversible.

n its general characteristics this adsorption curve is similar to that btained for silica gel. A desorption curve with similar characteristics

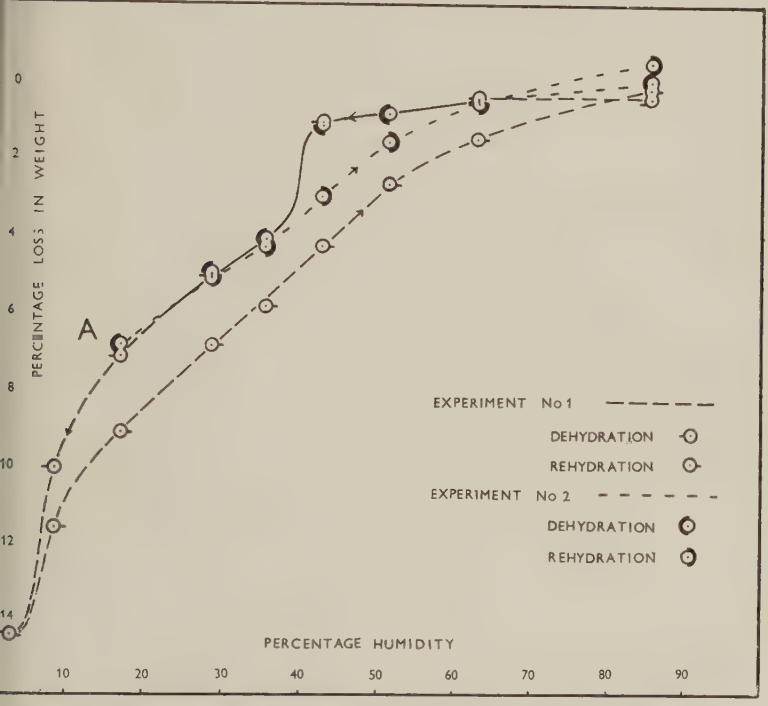

FIG. 3. Adsorption isotherms for plombierite gel. Temperature 16° C.

as been given by Giertz-Hedström for portland cement hydration roducts (1938, p. 517).

Complete analysis of the adsorption isotherms presented is not possible at present. It is evident, however, that the marked break in the esorption curves at 40 % relative humidity corresponds to the loss of large water fraction from equivalent energy positions within the gel ructure. Less generally this water may be regarded as occupying capillary system of defined dimensions within the gel. The X-ray idence already presented suggests that the gel pseudomorphs consist

of small orientated hydrate units and the possibilities of defined dim- sions in such a system are twofold. They may represent interla- distances in the hydrate units of structure, or the distance between t individual structural units. Regarded as a laminar capillary system, t classical theory, due to Kelvin, suggests that the spacing is of the orde of 10 Å. It has been found experimentally that the bulk volume of t gel does not change to an appreciable extent on complete dehydratio

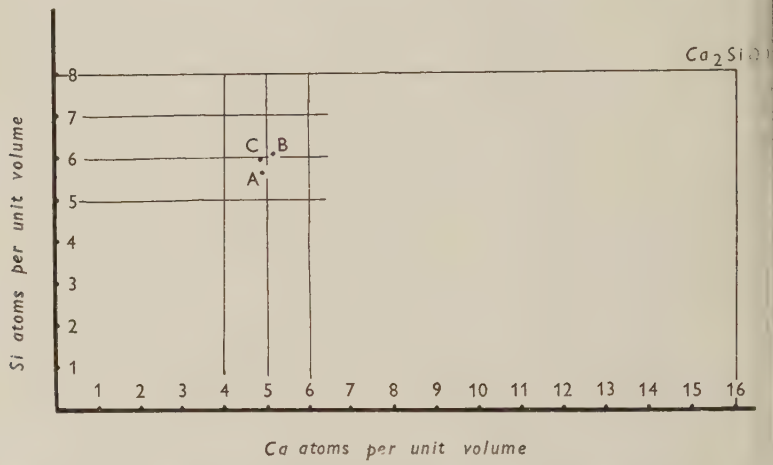

FIG. 4. The volume relationships of the hydration process. Points A, B, and C correspond to the analyses in table I.

THE VOLUME RELATIONSHIPS OF THE HYDRATION PROCESS.

The limits of variation in density and chemical composition of the gels have already been discussed, and it has been suggested that the process of hydration obtains at constant volume. The volume relationships of the process are represented in fig. 4, where the number of silicon and calcium atoms in unit volume of the parent silicate and the gel have been plotted. The unit volume chosen was that of half the unit cell of bredigite (Douglas, 1952, p. 882) or twice the volume of the larnite unit cell (Midgley, 1952, p. 307). From this diagram it is evident that the hydration process involves the removal of both calcium and silicon atoms from the structure, and that the volumetrical equivalent of half the bredigite unit cell contains 5 calcium and 6 silicon atoms. The formula unit of the crystalline hydrates of this group has the form $5CaO.6SiO_2.xH_2O$ (McConnell, 1954, 298), which suggests again that a

simple relationship may exist between the structure of the hydrate and that of the parent dicalcium silicate minerals.

Descriptions of silica hydrogels formed through the leaching of natural minerals have been given by a number of authors. In most cases some degree of ordering in the leached structure is observed. This is reflected in the retention of optical symmetry directions. Skeletonized apophyllite has been described by Bailey (1941, p. 565). In this case X-ray powder photographs showed that, in its structure, the silica hydrogel was essentially amorphous. Leaching experiments on gillespite ($BaFeSi_4O_{10}$) were carried out by Schaller (1929, p. 319) and later repeated by Pabst (1943, p. 388). The Fe and Ba atoms were removed from the mineral by acid leaching and the residual silica hydrogel formed was found to occupy the same volume as the parent silicate structure. A Laue photograph of a leached crystal of gillespite was taken by Pabst and this showed that the tetragonal symmetry of the parent silicate was preserved, but powder photographs of the silica hydrogel failed to show any reflections, indicating that the gel was amorphous.

A considerable amount of experimental work has been carried out on the hydration products of the portland cement clinker compounds β-Ca_2SiO_4 and Ca_3SiO_5. Both are known to hydrate at normal temperatures to give gelatinous hydration products. One of the most important of these is 'calcium silicate hydrate (I)', which, as noted previously in this paper, corresponds to the natural gelatinous mineral described in the present communication. The mechanism of gel formation, as outlined here, may have considerable bearing on the formation of calcium silicate hydrogels in the setting of portland cement.

Study of the natural materials suggests that such a hydrogel would be stable for an indefinite period of time in the presence of unhydrated clinker particles, and that, at high density, the gel would be competent to act as a rigid bonding medium in set cement.

Acknowledgements.—The author is indebted to the director of the Building Research Station, Garston, Herts., for permission to publish the analysis shown in table I. This research was carried out in the Department of Mineralogy and Petrology at Cambridge under the direction of Professor C. E. Tilley.

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EXPLANATION OF PLATE XVII.

Photomicrographs of larnite-rock and hydration products.

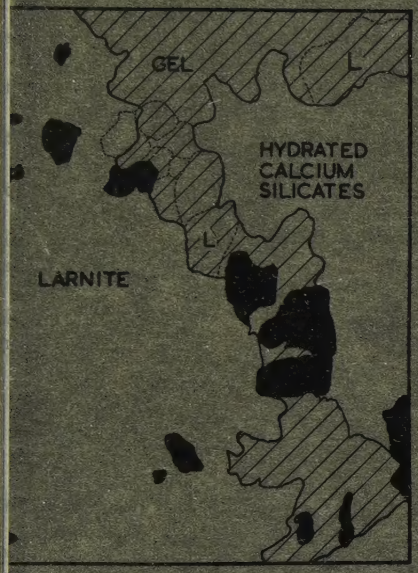
FIG. 1. Larnite-rock in thin section, showing a hydration zone of gel surrounding a vug containing afwillite and portlandite. ×85.

On the overlay the area of gelatinized larnite is shaded, and the outlines of some of the larnite crystals are indicated. Relict lamellar twinning is shown under crossed nicols (fig. 2) in the crystals marked L. The black areas are spinel.

FIG. 2. The same as of fig. 1 under crossed nicols showing the relict twinning in gel pseudomorphs after larnite. ×85.

FIG. 3. A crushed sample of plombierite gel from Scawt Hill. ×25.

FIG. 4. The same as fig. 3 under crossed nicols, showing birefringence effects in the gel. ×25.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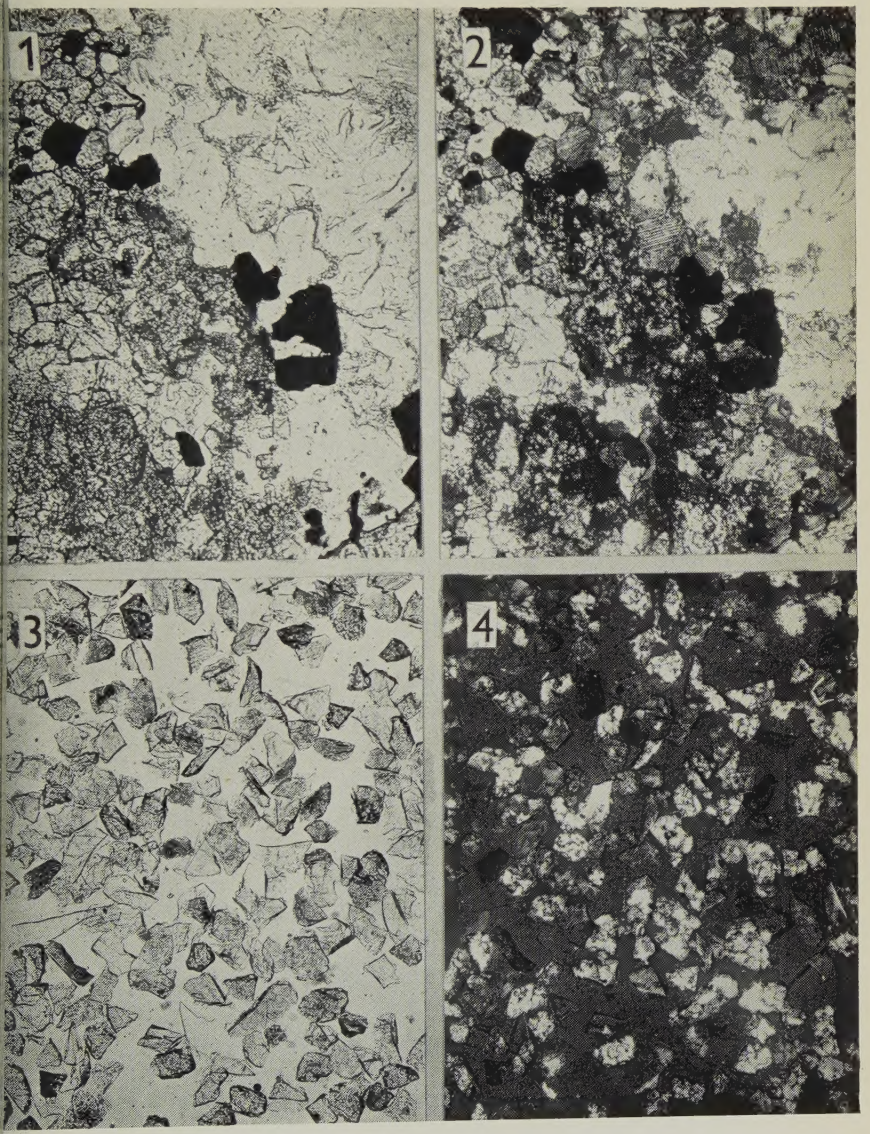

J. D. C. McConnell: Photomicrographs of larnite-rock and hydration products.